John L. Cadwalader.
Princeton College.

Senior Class.
Oct 18. 1855

(Fowner)

PKP

FOWNES'

MANUAL OF CHEMISTRY.

ELEMENTARY

CHEMISTRY,

THEORETICAL AND PRACTICAL.

BY

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EDITED, WITH ADDITIONS,

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A NEW AMERICAN,

FROM THE LAST AND REVISED LONDON EDITION.

WITH NUMEROUS ILLUSTRATIONS ON WOOD.

PHILADELPHIA:

BLANCHARD AND LEA.

1855.

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TO THE

NEW AMERICAN EDITION.

THE lamented death of the Author has caused the revision of this edition to fall into the hands of others, who have fully sustained its reputation by the additions which they have made, more especially in the portion devoted to Organic Chemistry, as set forth in their preface. This labour has been so thoroughly performed, that the American Editor has found but little to add, his notes consisting chiefly of such matters as the rapid advance of the science has rendered necessary, or of investigations which had apparently been overlooked by the Author's friends. These additions will be found distinguished by his initials.

The volume is therefore again presented as an exponent of the most advanced state of Chemical Science, and as not unworthy a continuation of the marked favour which it has received as an elementary text-book.

PHILADELPHIA,
October, 1853.

PREFACE.

The design of the present volume is to offer to the student commencing the subject of Chemistry, in a compact and inexpensive form, an outline of the general principles of that science, and a history of the more important among the very numerous bodies which Chemical Investigations have made known to us. The work has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to the larger and more comprehensive systematic works in our own language and in those of the Continent, and especially to prepare the student for the perusal of original memoirs, which, in conjunction with practical instruction in the laboratory, can alone afford a real acquaintance with the spirit of research and the resources of Chemical Science.

It has been my aim throughout to render the book as practical as possible, by detailing, at as great length as the general plan permitted, many of the working processes of the scientific laboratory, and by exhibiting, by the aid of numerous wood-engravings, the most useful forms of apparatus, with their adjustments and methods of use.

As one principal object was the production of a convenient and useful class-book for pupils attending my own lectures, I have been induced to adopt in the book the plan of arrangement followed in the lectures themselves, and to describe the non-metallic elements and some of their most important compounds before discussing the subject of the general philosophy of Chemical Science, and even

before describing the principle of the equivalent quantities, or explaining the use of the written symbolical language now universal among chemists. For the benefit of those to whom these matters are already familiar, and to render the history of the compound bodies described in the earlier part of the work more complete, I have added in foot-notes the view adopted of their Chemical constitution, expressed in symbols.

I have devoted as much space as could be afforded to the very important subject of Organic Chemistry; and it will, I believe, be found that there are but few substances of any general interest which have been altogether omitted, although the very great number of bodies to be described in a limited number of pages rendered it necessary to use as much brevity as possible.

GEO. FOWNES.

UNIVERSITY COLLEGE, LONDON,
October 5, 1847.

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TO THE

THIRD LONDON EDITION.

THE correction of this Edition for the press was the daily occupation of Professor Fownes, until a few hours previous to his death in January, 1849.

His wish and his endeavour, as seen in his manuscript, were to render it as perfect and as minutely accurate as possible.

When he had finished the most important part of the Organic Chemistry, where the most additions were required, he told me he should "do no more,"—he had "finished his work."

At his request I have corrected the press throughout, and made a few alterations that appeared desirable in the only part which he had left unaltered, the Animal Chemistry.

The index and the press have also been corrected throughout by his friend Mr. Robert Murray.

H. BENCE JONES, M.D.

80, GROSVENOR STREET,
Jan., 1850.

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TO THE

FOURTH LONDON EDITION.

It has been the endeavour of the Editors to include in the present edition of the Manual the progress of Chemistry since the Author's death.

The foundation which he laid, and the form which he gave to the work, remain untouched. But time has rendered it necessary that each portion should be revised; and a few repairs, and some considerable additions, especially in Organic Chemistry, have been made. Thus, several of the chapters on the Alcohols, the Organic Bases, Colouring Matters, &c., have been almost re-written.

Still, such changes only have been made as the Editors believed the Author himself would have desired, if his life had been spared to Science.

H. Bence Jones.
A. W. Hofmann.

London, *September*, 1852.

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MANUAL OF CHEMISTRY.

INTRODUCTION.

THE Science of Chemistry has for its object the study of the nature and properties of all the materials which enter into the composition or structure of the earth, the sea, and the air, and of the various organized or living beings which inhabit these latter. Every object accessible to man, or which may be handled and examined, is thus embraced by the wide circle of Chemical Science.

The highest efforts of Chemistry are constantly directed to the discovery of the general laws or rules which regulate the formation of chemical compounds, and determine the action of one substance upon another. These laws are deduced from careful observation and comparison of the properties and relations of vast numbers of individual substances;—and by this method alone. The science is entirely experimental, and all its conclusions the results of skilful and systematic experimental investigation.

The applications of the discoveries of Chemistry to the arts of life, and to the relief of human suffering in disease, are, in the present state of the science, both very numerous and very important, and encourage the hope of still greater benefits from more extended knowledge than that now enjoyed.

In ordinary scientific speech the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical*, which are not attended by such consequences. Changes of decomposition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and the attractive forces, whose laws and effects lie within the province of Physics or Natural Philosophy.

Nearly all the objects presented by the visible world are of a compound nature, being chemical compounds, or variously disposed mixtures of chem-

ical compounds, capable of being resolved into simpler forms of matter. Thus, a piece of limestone or marble by the application of a red-heat is decomposed into quicklime and a gaseous body, carbonic acid. Both lime and carbonic acid are in their turn susceptible of decomposition, the first into a metal, calcium, and oxygen, and the second into carbon and oxygen. For this purpose, however, simple heat does not suffice, the resolution of these substances into their components demanding the exertion of a high degree of chemical energy. Beyond this second step of decomposition the efforts of Chemistry have hitherto been found to fail, and the three bodies, calcium, carbon, and oxygen, having resisted all attempts to resolve them into simpler forms of matter, are accordingly admitted into the list of *elements*;—not from any belief in their real oneness of nature, but from the absence of any evidence that they contain more than one description of matter.

The partial study of certain branches of Physical Science, as the physical constitution of gases, the chief phenomena of heat and electricity, and a few other subjects, forms such an indispensable introduction to Chemistry itself, that it is never omitted in the usual courses of oral instruction. A sketch of these subjects is, in accordance with these views, placed at the commencement of the present volume.

PART I.—PHYSICS.

OF DENSITY AND SPECIFIC GRAVITY.

It is of great importance in the outset to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density of a body* is meant its *mass*, or *quantity of matter*, compared with the mass or quantity of matter of an *equal volume* of some standard body, arbitrarily chosen. *Specific gravity* denotes the *weight* of a body, as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity.[1] In all cases of solids and liquids this standard of unity is pure water at the temperature of 60° Fahr. (15°·5C). Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable; it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of perfect purity. The ordinary expression of specific weight, therefore, is a number expressing how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say that concentrated oil of vitriol has a specific gravity equal to 1·85, or that perfectly pure alcohol has a density of 0·794 at 60°, we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1·85, 0·794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature; for, as will be hereafter shown, liquids are extremely expansible by heat; otherwise, a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the specific gravity of liquids is determined; this is the simplest case, and the one which best illustrates the general principle.

In order to obtain at pleasure the specific gravity of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by the weight of the water; the quotient will of course be greater or less than unity, as the liquor experimented on is heavier or lighter than water. Now, to weigh equal bulks of two fluids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions, a condition very easy of fulfilment.

A thin glass bottle, or flask, with a narrow neck, is procured, of the figure represented on the next page, (fig. 1), and of such capacity as to contain, when filled to about half-way up the neck, exactly 1000 grains of distilled water at 60° (15°·5C). Such a flask is readily procured from any one of the Italian artificers, to be found in every large town, who manufacture cheap thermometers for sale. A counterpoise of the exact weight of the empty

[1] In other words, density means comparative *mass*, and specific gravity comparative *weight*. These expressions, although really relating to distinct things, are often used quite indifferently in chemical writings, and without practical inconvenience, since mass and weight are directly proportional to each other.

Fig. 1.

bottle is made from a bit of brass, an old weight, or something of the kind, and carefully adjusted by filing: an easy task. The bottle is then graduated, by introducing water at 60°, until it exactly balances the 1000-grain weight and counterpoise in the opposite scale; the height at which the water stands in the neck is marked by a scratch, and the instrument is complete for use. The liquid to be examined is brought to the temperature of 60°, and with it the bottle is filled up to the mark before mentioned; it is then weighed, the counterpoise being used as before, and the specific gravity directly ascertained.

A watery liquid in a narrow glass tube always presents a curved surface from the molecular action of the glass, the concavity being upwards. It is better, on this account, in graduating the bottle, to make two scratches as represented in the drawing, one at the top and the other at the bottom of the curve: this prevents any future mistake. The marks are easily made by a fine, sharp, three-square file, the hard point of which, also, it may be observed, answers perfectly well for writing upon glass, in the absence of a proper diamond-pencil.

The specific-gravity bottle above described differs from those commonly made for sale by the instrument-makers. These latter are constructed with a perforated stopper, so arranged that when the bottle is quite filled, the stopper put in its place, and the excess of liquid which flows through the hole wiped from the outside, a constant measure is always had. There are inconveniences attending the use of the stopper which lead to a preference of the open bottle with merely a mark on the neck, even when very volatile liquids are experimented with.

It will be quite obvious that the adoption of a flask holding exactly 1000 grains of water has no other object than to save the trouble of a very trifling calculation; any other quantity would answer just as well, and, in fact, the experimental chemist is often compelled to use a bottle of much smaller dimensions, from scarcity of the liquid to be examined. The shape is also in reality of little moment; any light phial with a narrow neck may be employed, not quite so conveniently perhaps, as a specific-gravity bottle.

The determination of the specific gravity of a solid is also an operation of great facility, although the principle is not so obvious. As it would be impossible to put in practice a direct method like that indicated for liquids, recourse is had to another plan. The celebrated theorem of Archimedes affords a solution of the difficulty. This theorem may be thus expressed:—

> When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces; that is, to the weight of its own bulk of that fluid.

It is easy to give experimental proof of this very important proposition, as well as to establish it by reasoning. The drawing (fig. 2) represents a little apparatus for the former purpose. This consists of a thin cylindrical vessel of brass, into the interior of which fits very accurately a solid cylinder of the same metal, thus exactly filling it. When the cylinder is suspended beneath the bucket, as seen in the sketch, the whole hung from the arm of a balance and counterpoised, and then the cylinder itself immersed in water, it will be found to have lost a certain weight; and that this loss is precisely equal to the weight of an equal bulk of water, may then be proved by filling

he bucket to the brim, whereupon the equilibrium will be restored.

The consideration of the great hydrostatic law of fluid pressure easily proves the truth of the principle laid down. Let the reader figure to himself a vessel of water, having immersed in it a solid cylindrical or rectangular body, and so adjusted with respect to density, that it shall float indifferently in any part beneath the surface (fig. 3).

Now the law of fluid pressure is to this effect:—The pressure exerted by a fluid upon the containing vessel, or upon anything plunged beneath its surface, depends, first, upon the density of that fluid, and, secondly, upon the perpendicular height of the column. It is independent of the form and lateral dimensions of the vessel or immersed body. Moreover, owing to the peculiar physical constitution of fluids, this pressure is exerted equally in every direction, upwards, downwards, and laterally, with equal force.

The floating body is in a state of equilibrium; therefore the pressure downwards caused by its gravitation must be exactly compensated by the upward transmitted pressure of the column of water *a*, *b*.

But this pressure downwards is obviously equal to the weight of an equal quantity of water, since the body of necessity displaces its own bulk—

Hence, the weight lost, or supported by the water, is the weight of a volume of water equal to that of the body immersed.

Whatever be the density of the substance it will be buoyed up to this amount; in the case supposed, the buoyancy is equal to the whole weight of the body, which is thus, while in the water, reduced to nothing.

A little reflection will show that the same reasoning may be applied to a body of irregular form; besides, a solid of any figure may be divided by the imagination, into a multitude of little perpendicular prisms, or cylinders, to each of which the argument may be applied. What is true of each individually, must necessarily be true of the whole together.

This is the fundamental principle; its application is made in the following manner: Let it be required, for example, to know the specific gravity of a body of extremely irregular form, as a small group of rock-crystals: the first part of the operation consists in determining its absolute weight, or, more correctly speaking, its weight in air; it is next suspended from the balance-pan by a fine horse-hair, immersed completely (fig. 4) in pure water at 60° (15°·5C), and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, the weight of an equal bulk. This being known, nothing more is required than to find, by division, how many

Fig. 2.

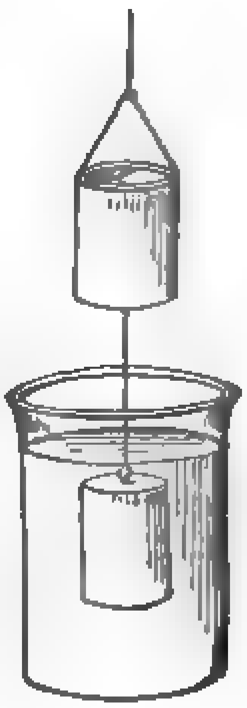


Fig. 3.

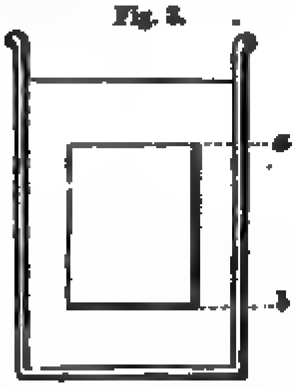
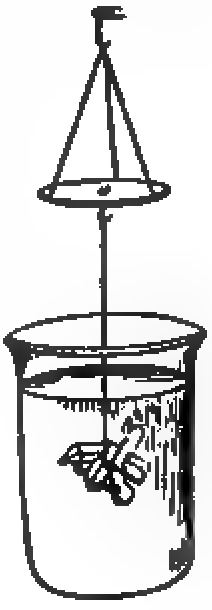


Fig. 4.



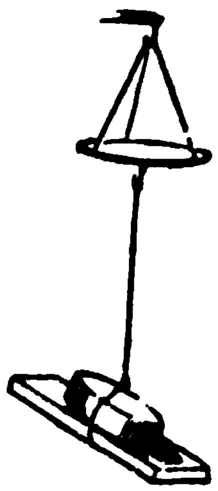
times the latter number is contained in the former; the quotient will be the density, water being taken = 1. For example:—

The quartz-crystals weigh in air	293·7 grains.
When immersed in water, they weigh	180·1
Difference being the weight of an equal volume of water	113·6

$$\frac{293 \cdot 7}{113 \cdot 6} = 2 \cdot 58, \text{ the specific gravity required.}$$

The arbitrary rule is generally thus written: "Divide the weight in air by the loss of weight in water, and the quotient will be the specific gravity." In reality, it is not the weight in air which is required, but the weight the body would have in empty space: the error introduced, namely, the weight of an equal bulk of air, is so trifling that it is usually neglected.

Fig. 5.



Sometimes the body to be examined is lighter than water, and floats. In this case it is first weighed and afterwards attached to a piece of metal (fig. 5), heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the specific gravity, as will be at once seen by the following example:—

Light substance (a piece of wax) weighs in air	133·7 grains.
Attached to a piece of brass, the whole now weighs	183·7
Immersed in water, the system weighs	38·8
Weight of water equal in bulk to brass and wax	144·9
Weight of brass in air	50·0
Weight of brass in water	44·4
Weight of equal bulk of water	5·6
Bulk of water equal to wax and brass	144·9
Bulk of water equal to brass alone	5·6
Bulk of water equal to wax alone	139·3

$$\frac{133 \cdot 7}{139 \cdot 3} = 0 \cdot 9598.$$

In all such experiments, it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air-bubbles; otherwise a false result will be obtained.

Other cases require mention in which these operations must be modified to meet particular difficulties. One of these happens when the substance is dissolved or acted upon by water. This difficulty is easily conquered by substituting some other liquid of known density which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the specific gravity of crystallized sugar is required, we proceed in the following way:—The specific gravity of the oil of turpentine is first carefully determined; let it be 0·87;

the sugar is next weighed in the air, then suspended by a horse-hair, and weighed in the oil; the difference is the weight of an equal bulk of the latter; a simple calculation gives the weight of a corresponding volume of water:—

Weight of sugar in air	400	grains.
Weight of sugar in oil of turpentine	182·5	
Weight of equal bulk of oil of turpentine	217·5	

$$87 : 100 = 217{\cdot}5 : 250,$$

the weight of an equal bulk of water; hence the specific gravity of the sugar,

$$\frac{400}{250} = 1{\cdot}6.$$

The substance to be examined may be in small fragments, or powder. Here the operation is also very simple. A bottle holding a known weight of water is taken; the specific-gravity bottle already described answers perfectly well. A convenient quantity of the substance is next carefully weighed out, and introduced into the bottle, which is then filled up to the mark on the neck with distilled water. It is clear that the vessel now contains less water by a quantity equal to the bulk of the powder than if it were filled in the usual manner. It is, lastly, weighed. In the subjoined experiment emery powder was tried.

The bottle held, of water	1000	grains.
The substance introduced weighed	100	
Weight of the whole, had no water been displaced	1100	
The observed weight is, however, only	1070	
Hence water displaced, equal in bulk to the powder	30	

$$\frac{100}{30} = 3{\cdot}333 \text{ specific gravity.}$$

By this method the specific gravities of metals in powder, metallic oxides, and other compounds, and salts of all descriptions, may be determined with great ease. Oil of turpentine may be used with most soluble salts. The crystals should be crushed or roughly powdered to avoid errors arising from cavities in their substance.

The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an application is made in the common hydrometer,—an instrument for finding the specific gravities of liquids in a very easy and expeditious manner.

When a solid body is placed upon the surface of a fluid specifically heavier than itself, it sinks down until it displaces a quantity of fluid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose specific weight is one-half that of the fluid, the position of equilibrium will involve the immersion of exactly one-half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a fluid of one-half the specific gravity of water, if such could be found, then it would sink beneath the surface, and remain indifferently in any part. A floating body of known specific gravity may thus be used as an indicator of the specific gravity of a fluid. In this manner little glass beads (fig. 6) of known specific gravities are sometimes employed in the arts to ascertain in a rude manner the specific gravity of liquids;

Fig. 6.

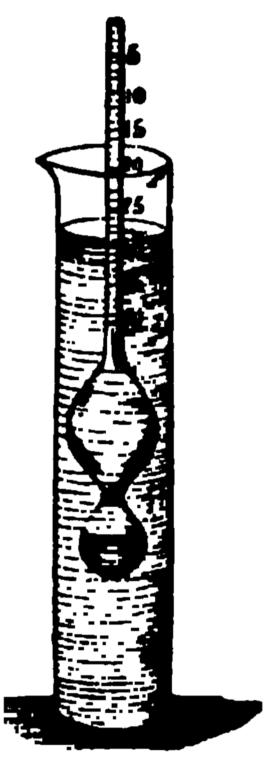
...ne that floats indifferently beneath the surface, without either sinking ...rising has of course the same specific gravity as the liquid itself; this is ...inted out by the number marked upon the bead.

Fig. 7.

The hydrometer (fig. 7) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The use of the instrument is very simple. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of fluid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Very extensive use is made of instruments of this kind in the arts; these sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the specific gravity by the aid of tables of comparison drawn up for the purpose.

Fig. 8.



A very convenient and useful instrument in the shape of a small hydrometer (fig. 8) for taking the specific gravity of urine, has lately been put into the hands of the physician;[1] it may be packed into a pocket-case, with a little jar and a thermometer, and is always ready for use.[2]

The determination of the specific gravity of gases and vapours of volatile liquids is a problem of very great practical importance to the chemist; the theory of the operation is as simple as when liquids themselves are concerned, but the processes are much more delicate, and involve besides certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper to defer the consideration of these matters for the present. The method of determining the specific gravity of a gas will be found described under the head of

[1] ...his and other instruments described or figured in the course of the work, may be had ... Newman, 122 Regent Street, upon the excellence of whose workmanship reliance may ...ly placed.

[2] ...he graduation of the urinometer is such that each degree represents 1-1000, thus ...; the actual specific gravity without calculation, for the number of degrees on the ...out by the surface of the liquid when this instrument is at rest, added to 1000 will ...ent the density of the liquid. If, for example, the surface of the liquid coincide with ... the scale, the specific gravity will be 1023, about the average density of healthy —h B

"Oxygen," and that of the vapour of a volatile liquid in the Introduction to Organic Chemistry.[1]

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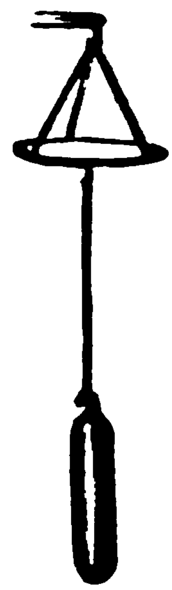
[1] The mode of determining the specific gravity of a liquid by means of a solid has been omitted in the text. It results from the theorem of Archimedes, that if any solid be immersed in water and then in any other liquid, the loss of weight sustained in each case will give the relative weights of equal bulks of the liquids, and on dividing the weight of the liquid by the weight of the water, the quotient will be the specific gravity of the liquid experimented on. For instance, let a piece of glass rod be suspended from the balance-pan and exactly counterpoised, then immerse it in water and restore the equipoise by weights added to the pan to which the glass is suspended, the amount will give the loss of weight by immersion or the weight of a bulk of water equal to that of the rod. Now wipe the glass dry, and having removed the additional weights, immerse it in the other liquid, and restore the equipoise as before; this latter weight is the weight of a bulk of the liquid equal to that of the water. The latter divided by the former gives the specific gravity. For example:—

The glass rod loses by immersion in water .... 171 grains.

The glass rod loses by immersion in alcohol 143

$\frac{143}{171}=\cdot 836$ the specific gravity required.—R. B.

Fig. 2.



OF THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE, AND OF GASES IN GENERAL.

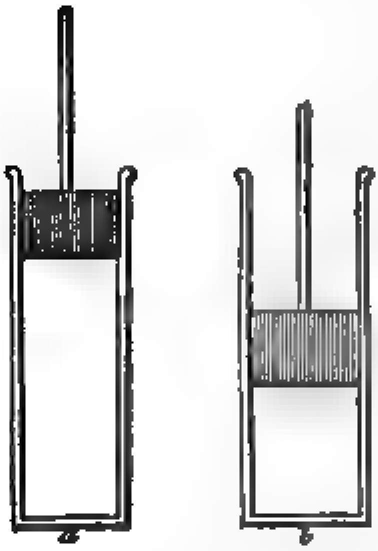
It requires some little abstraction of mind to realize completely the singular condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelopes everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of an extremely valuable instrument, the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, fig. 10, closed at the bottom, in which moves a piston, air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Fig. 10.



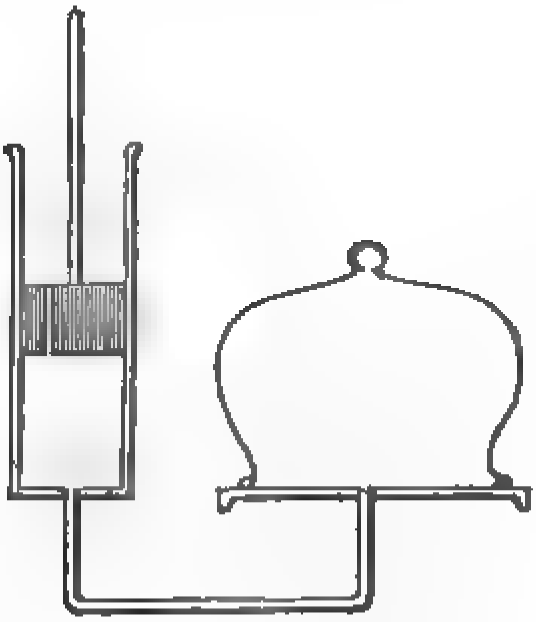
Again, take *b*, fig. 10, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the enclosed space, and this to an apparently unlimited extent. A volume of air which under ordinary circumstances occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part; the vessel is *full*, although the gas is in a state of extreme tenuity. This power of expansion which air possesses may have, *and probably has*, in reality, a limit; but the limit is never reached in

practice. We are quite safe in the assumption, that, for all purposes of experiment, however refined, air is perfectly elastic.

It is usual to assign a reason for this indefinite expansibility by ascribing to the particles of material bodies, when in a gaseous state, a self-repulsive energy. This statement is commonly made somewhat in this manner: matter is under the influence of two opposite forces, one of which tends to draw the particles together, the other to separate them. By the preponderance of one or other of these forces, we have the three states called solid, liquid, and gaseous. When the particles of matter, in consequence of the direction and strength of their mutual attractions, possess only a very slight power of motion, a solid substance results; when the forces are nearly balanced, we have a liquid, the particles of which in the interior of the mass are free to move, but yet to a certain extent are held together; and, lastly, when the attractive power seems to be completely overcome by its antagonist, we have a gas or vapour.

Various names are applied to these forces, and various ideas entertained concerning them; the attractive forces bear the name of cohesion when they are exerted between particles of matter separated by a very small interval, and gravitation, when the distance is great. The repulsive principle is often thought to be identical with the principle of heat.

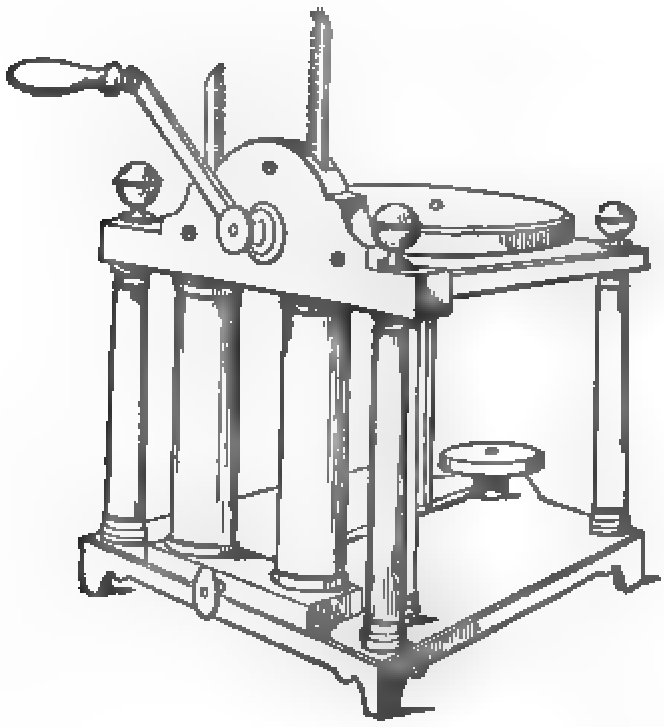
Fig. 11.



The ordinary air-pump, shown in section in fig. 11, consists essentially of a metal cylinder, in which moves a tightly-fitting piston, by the aid of its rod. The bottom of the cylinder communicates with the vessel to be exhausted, and is furnished with a valve opening upwards. A similar valve, also opening upwards, is fitted to the piston; these valves are made with slips of oiled silk. When the piston is raised from the bottom of the cylinder, the space left beneath it must be void of air, since the piston-valve opens only in one direction; the air within the receiver having on that side nothing to oppose its elastic power but the weight of the little valve, lifts the latter, and escapes into the cylinder. So soon as the piston begins to descend, the lower valve closes, by its own weight, or by the transmitted pressure from above, and communication with the receiver is cut off. As the descent of the piston continues, the air included within the cylinder be-

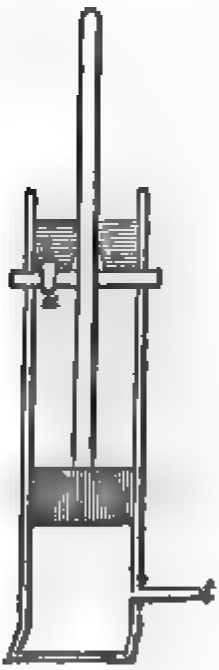
comes compressed, its elasticity is increased, and at length it forces open the upper valve, and escapes into the atmosphere. In this manner, a cylinder full of air is at every stroke of the pump removed from the receiver. During the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

Fig. 12.



In practice, it is very convenient to have two such barrels or cylinders, arranged side by side, the piston-rods of which are formed into racks, having a pinion, or small-toothed wheel, between them, moved by a winch. By this contrivance the operation of exhaustion is much facilitated and the labour lessened. The arrangement is shown in fig. 12.

Fig. 13.



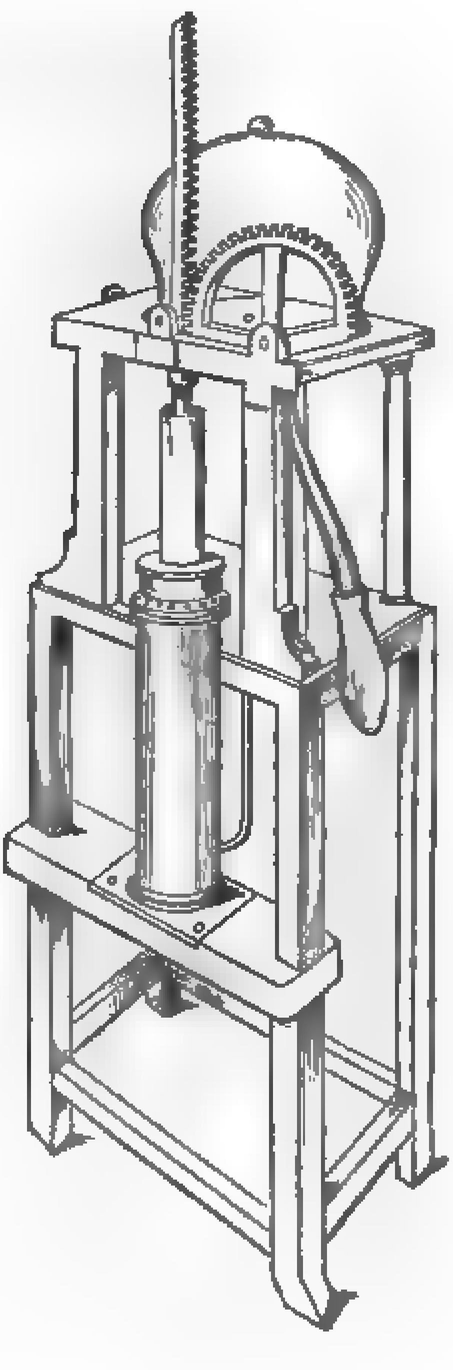
A simpler and far superior form of air-pump is thus constructed: the cylinder, which may be of large dimensions, is furnished with an accurately-fitted solid piston, the rod of which moves, air-tight, through a contrivance called a stuffing-box, at the top of the cylinder, where also the only valve *essential* to the apparatus is to be found; the latter is a solid conical plug of metal, shown at *a* in the figure, kept tight by the oil contained in the chamber into which it opens. The communication with the vessel to be exhausted is made by a tube which enters the cylinder a little above the bottom. The action is the following: let the piston be supposed in the act of rising from the bottom of the cylinder; as soon as it passes the mouth of the tube *t*, all communication is stopped between the air above the piston and the vessel to be exhausted; the enclosed air suffers compression, until it acquires sufficient elasticity to lift the metal valve and escape by bubbling through the oil. When the piston makes its descent, and this valve

closes, a vacuum is left in the upper part of the cylinder, into which the air of the receiver rushes so soon as the piston has passed below the orifice of the connecting tube.

In the silk-valved air-pump, exhaustion ceases when the elasticity of the air in the receiver becomes too feeble to raise the valve; in that last described, the exhaustion may, on the contrary, be carried to an indefinite extent, without, however, under the most favourable circumstances, becoming complete. The conical valve is made to project a little below the cover of the cylinder, so as to be forced up by the piston when the latter reaches the top of the cylinder; the oil then enters and displaces any air that may be lurking in the cavity.

It is a great improvement to the machine to supply the piston with a *relief-valve* opening upwards; this may also be of metal, and contained within the body of the piston. Its use is to avoid the momentary condensation of the air in the receiver when the piston descends. The pump is worked by a lever in the manner represented in fig. 14.

Fig. 14.



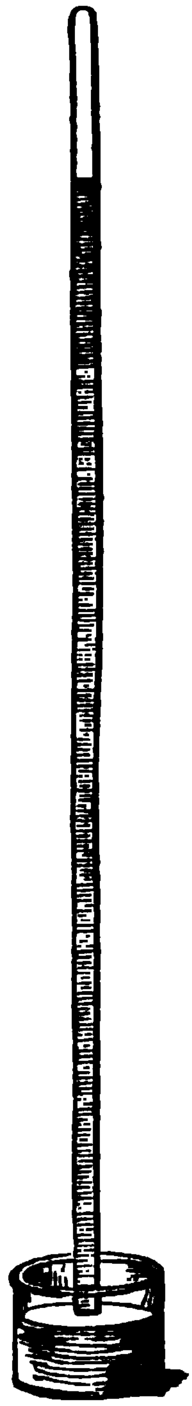
To return to the atmosphere. Air possesses weight: a light flask or globe of glass, furnished with a stop-cock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, this difference may amount to nearly 30 grains.

The mere fact of the pressure of the atmosphere may be demonstrated by securely tying a piece of bladder over the mouth of an open glass receiver, and then exhausting the air from beneath it; the bladder will become more and more concave, until it suddenly breaks. A thin square glass bottle, or a large air-tight tin box, may be crushed by withdrawing the support of the air in the inside. Steam-boilers have been often destroyed in this manner by collapse, in consequence of the accidental formation of a partial vacuum within.

After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one *of its ends dipping into* a vessel of liquid,

Fig. 15.



the latter, on being allowed access to the tube, would rise in its interior until the weight of the column balanced the pressure of the air upon the surface of the liquid. Now if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere. Such an instrument is the barometer: a straight glass tube is taken, about 36 inches in length, and sealed by the blow-pipe flame at one extremity; it is then filled with clean, dry mercury, care being taken to displace all air-bubbles, the open end stopped with a finger, and the tube inverted in a basin of mercury. On removing the finger, the fluid sinks away from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, and balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury 30 inches in height, or thereabouts; now such a column, having an area of one inch, weighs between 14 and 15 pounds, consequently such must be the amount of the pressure exerted upon every square inch of the surface of the earth, and of the objects situated thereon, at least near the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction, and it may be doubled, or even tripled without injury.

A barometer may be constructed with other liquids besides mercury; but, as the height of the column must always bear an inverse proportion to the density of the liquid, the length of tube required will be often considerable; in the case of water it will exceed 33 feet. It is seldom that any other liquid than mercury is employed in the construction of this instrument. The Royal Society of London possess a water-barometer at their apartments at Somerset House. Its construction was attended with great difficulties, and it has been found impossible to keep it in repair.

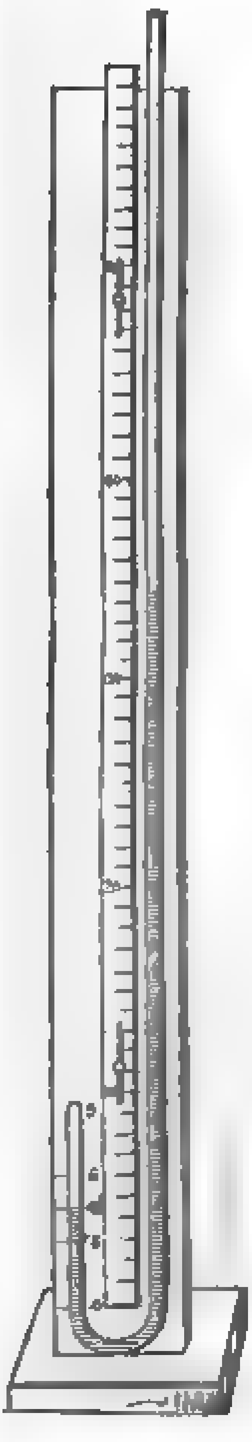
It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and which is thus expressed:—

> The volume of a gas is *inversely* as the pressure; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one-half, and shrink, on the contrary, to 50 cubic inches if the original pressure were doubled. The change of density must necessarily be in the inverse proportion to that of the volume, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, is easily demonstrable by direct experiment. A glass tube, about 7 feet in length, is closed at one end, and bent into the form shown in fig. 16, the open limb of the siphon being the longest. It is next attached to a board furnished with a moveable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until it is found that the inclosed air has been reduced to one-half of its former volume; and on applying the scale it will be found that the level

Fig. 18.



e mercury in the open part of the tube stands nearly 30 inches above that in the closed portion. pressure of an additional "atmosphere" has con-ently reduced the bulk of the contained air to ialf. If the experiment be still continued until olume of air is reduced to a third, it will be found the column measures 60 inches, and so in like ortion as far as the experiment is carried.

e above instrument is better adapted for illustra-of the principle than for furnishing rigorous proof e law; this has, however, been done. MM. Arago Dulong published, in the year 1830, an account of in experiments made by them in Paris, in which aw in question had been verified to the extent of mospheres.

l gases are alike subject to this law, and all va-s of volatile liquids, when remote from their points quefaction.[1] It is a matter of the greatest im-ance in practical chemistry, since it gives the is of making corrections for pressure, or deter-ng by calculation the change of volume which a gas d suffer by any given change of external pressure. t it be required, for example, to solve the fol-g problem:—We have 100 cubic inches of gas in iduated jar, the barometer standing at 29 inches; many cubic inches will it occupy when the column to 30 inches?—Now the volume must be inversely e pressure; consequently a change of pressure in proportion of 29 to 30 must be accompanied by inge of volume in the proportion of 30 to 29; 30 : inches of gas contracting to 29 cubic inches r the conditions imagined. Hence the answer:

$$30 : 29 = 100 : 96{\cdot}67 \text{ cubic inches.}$$

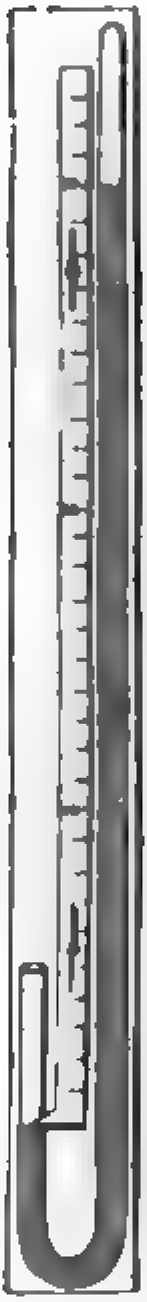
reverse of the operation will be obvious. The tical pupil will do well to familiarize himself with simple calculations of correction for pressure.

om what has been said respecting the easy com-ibility of gases, it will be at once seen that the sphere cannot have the same density, and cannot equal pressures at different elevations above the evel, but that, on the contrary, these must diminish the altitude, and very rapidly. The lower strata r have to bear the weight of those above them; become, in consequence, deeper and more com-ed than the upper portions. The following table, is taken from Prof. Graham's work, shows in a very simple manner ule followed in this respect.

Height above the sea, in miles.	Volume of air.	Height of barometer, in inches.
0	1	30
2·705	2	15
5·41	4	7·5
8·115	8	3·75
10·82	16	1·875
13·525	32	0·9375
16·23	64	0·46875

[1] hen near the liquefying point the law no longer holds; the volume diminishes more than the theory indicates, a smaller amount of pressure being then sufficient.

Fig. 17.



The numbers in the first column form an *arithmetica* by the constant addition of 2·705; those in the second ec increasing *geometrical* series, each being the double of it cessor; and those in the third, a decreasing geometrica in which each number is the half of that standing abov ascending in the air in a balloon, these effects are served; the expansion of the gas within the machine, fall of the mercury in the barometer, soon indicate to t ger the fact of his having left below him a considerable the whole atmosphere.

The invention of the barometer, which took place in 1643, by Torricelli, a pupil of the celebrated Galileo, led to the observation that the atmospheric pressure same level is not constant, but possesses, on the cor small range of variation, seldom exceeding in Europe inches, and within the tropics usually confined withi narrower limits. Two kinds of variations are disting regular or horary, and irregular or accidental. It i observed, that in Europe the height of the barometer is at two periods in the twenty-four hours, depending u season. In winter, the first maximum takes place about the first minimum at 3 P.M., after which the mercu rises and attains its greatest elevation at 9 in the eve summer these hours of the aërial tides are somewhat The accidental variations are much greater in amou render it extremely difficult to trace the regular chang mentioned.

The barometer is applied with great advantage to t surement of accessible heights, and it is also in daily foretelling the state of the weather; its indications are respect extremely deceptive, except in the case of sudd violent storms, which are almost always preceded by fall in the mercurial column. It is often extremely u this respect at sea.

To the practical chemist, a moderately good baromet indispensable article, since in all experiments in which of gases are to be estimated, an account must be taken pressure of the atmosphere. The marginal drawing re a very convenient and economical siphon barometer purpose. A piece of new and stout tube, of about one-t an inch in internal diameter, is procured at the glass sealed at one extremity, and bent into the siphon form, a sented. Pure and warm mercury is next introduced by successive p until the tube is completely filled, and the latter being held in an position, the level of the metal in the lower and open limb is conve adjusted by displacing a portion by a stick or glass rod. The barom lastly, attached to a board, and furnished with a long scale, made which may be of box-wood, with a slip of ivory at each end. When servation is to be taken, the lower extremity or zero of the scale is exactly even with the mercury in the short limb, and then the heigh column at once read off.

HEAT.

It will be convenient to consider the subject of Heat under several sections, and in the following order:—

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Change of state.
4. Capacity of bodies for heat.

The phenomena of radiation must be deferred until a sketch has been given of the science of light.

EXPANSION.

If a bar of metal (fig. 18) be taken, of such magnitude as to fit accurately to a gauge when cold, heated considerably, and again applied to the guage, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb (fig. 19), furnished with a narrow neck, be plunged into hot water, or exposed to any other

Fig. 18.

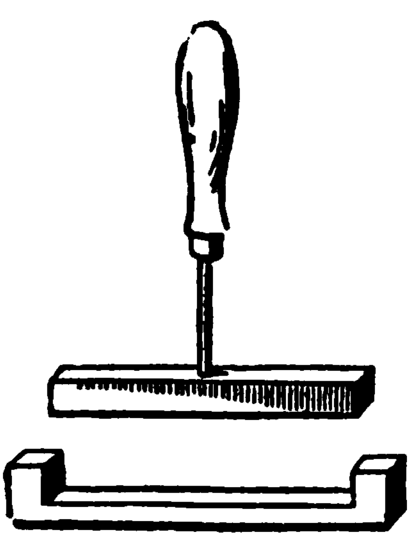


Fig. 19.

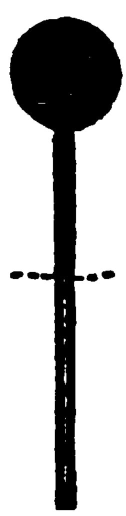
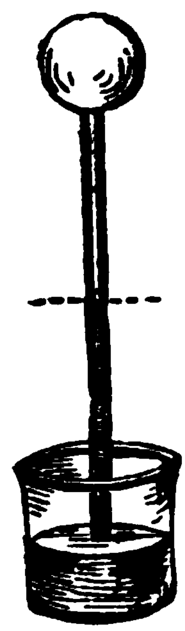


Fig. 20.



source of heat, the liquid will mount in the stem, showing that its volume has been increased.

Or, if a portion of air be confined in any vessel (fig. 20), the application of a slight degree of heat will suffice to make it occupy a space sensibly larger.

This most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed capable of taking cognizance of changes of temperature in a manner equally accurate and convenient: such an instrument is the thermometer.

A capillary glass tube is chosen, of uniform diameter: one extremity is closed and expanded into a bulb, by the aid of the blowpipe flame, and the

other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit lamp, and the open extremity plunged into a vessel of mercury, a portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapour, on the condensation of which the metal is forced into the instrument by the pressure of the air, until it becomes completely filled. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top; and then the extremity of the tube is hermetically sealed by the blowpipe. The retraction of the mercury on cooling now leaves an empty space in the upper part of the tube, which is essential to the perfection of the instrument.

The thermometer has yet to be graduated; and to make its indications comparable with those of other instruments, a scale, having certain fixed points, at the least two in number, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described, and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing-point of water, or melting-point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling-point of water, which is always the same under similar circumstances. A clean metallic vessel is taken, into which pure water is put and made to boil; a thermometer placed in the boiling liquid just so deep as is necessary to cover the bulb, invariably marks the same degree of temperature so long as the height of the barometer remains unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees; this is entirely arbitrary. In the greater part of Europe and in America, the scale called *centigrade* is employed; the space in question being divided into 100 parts, the zero being placed at the freezing point of water. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England the very inconvenient division of Fahrenheit is still in use; the above space is divided into 180 degrees, but the zero, instead of starting from the freezing-point of water, is placed 32 degrees below it, so that the temperature of ebullition is expressed by the number 212°.

The plan of Reaumur is nearly confined to a few places in the north of Germany and to Russia; in this scale the freezing-point of water is made 0°, and the boiling-point 80°.

It is unfortunate that an uniform system has not been generally adopted in graduating thermometers; this would render unnecessary the labour which now so frequently has to be performed of translating the language of one scale into that of another. To effect this, presents, however, no great difficulty. Let it be required, for example, to know the degree of Fahrenheit's scale which corresponds to 60° centigrade.

$$100^\circ \text{ C.} = 180^\circ \text{ F., or } 5^\circ \text{ C.} = 9^\circ \text{ F.}$$

Consequently,

$$5 : 9 = 60 : 108.$$

then, as Fahrenheit's scale commences with 32° instead of 0°, that ɪer must be added to the result, making 60° C. = 140° F.

e rule then will be the following:—To convert centigrade degrees into enheit degrees, multiply by 9, divide the product by 5, and add 32; to ɪrt Fahrenheit degrees into centigrade degrees, subtract 32, multiply and divide by 9.

e reduction of negative degrees, or those below zero of either scale, nts rather more apparent difficulty; a little consideration, however, render the method obvious, the interval between the two zero-points ; borne in mind.

ɪrcury is usually chosen for making thermometers, on account of its arity of expansion within certain limits, and because it is easy to have cale of great extent, from the large interval between the freezing and ɪg-points of the metal. Other substances are sometimes used; alcohol ployed for estimating very low temperatures.

:-thermometers are also used for some few particular purposes; indeed, rst thermometer ever made was of this kind. There are two modifica- of this instrument; in the first, the liquid into which the tube dips is to the air, and in the second (fig. 21), the atmosphere is completely ɪded. The effects of expansion are in the one case complicated with arising from changes of pressure, and in the other cease to be visible when the whole instrument is subjected to alterations of temperature, ɪse the air in the upper and lower reservoir, being equally affected by changes, no alteration in the height of the fluid column can occur. rdingly, such instruments are called *differential* thermometers, since serve to measure differences of temperatures between the two portions r, while changes affecting both alike are not indicated. Fig. 22 shows ɪer form of the same instrument.

Fig. 21.

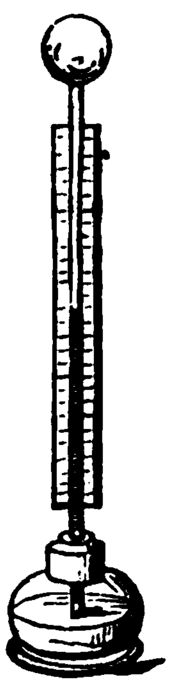
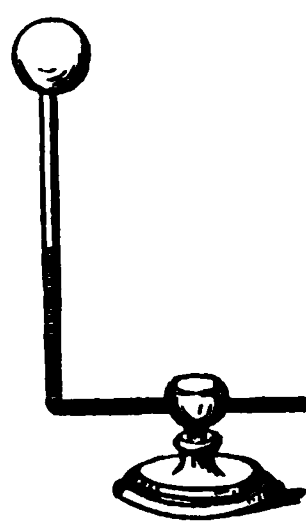


Fig. 22.



ɪe air-thermometer may be employed for measuring all temperatures, the lowest to the highest; M. Pouillet has described one by which the of an air-furnace could be measured. The reservoir of this instrument platinum, and it is connected with a piece of apparatus by which the ɪase of volume experienced by the included air is determined.

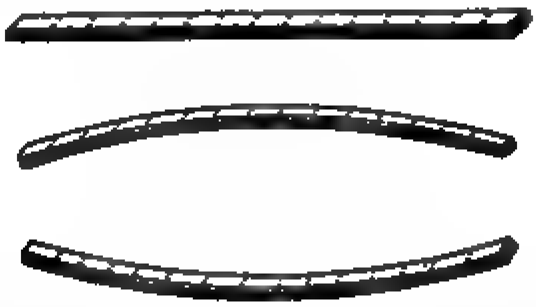
ll bodies *are enlarged* in their dimensions by the application of heat, *reduced by its abstraction*, or, in other words, contract on being artifi-

cially cooled; this effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases.

Each solid and liquid has a rate of expansion peculiar to itself; gases, on the contrary, all expand alike for the same increase of heat.

The difference of expansibility among solids is very easily illustrated by the following arrangement: a thin straight bar of iron is firmly fixed by numerous rivets, to a similar bar of brass; so long as the temperature at which the two metals were united remains unchanged, the compound bar preserves its straight figure; but any alteration of temperature gives rise to a corresponding curvature. Brass is more dilatable than iron; if the bar be heated, therefore, the former expands more than the latter, and forces the straight bar into a curve, whose convex side is the brass; if it be artificially cooled, the brass contracts more than the iron, and the reverse of this effect is produced.

Fig. 23.



This fact has received a most valuable application. It is not necessary to insist on the importance of possessing instruments for the accurate measurement of time; such are absolutely indispensable to the successful cultivation of astronomical science, and not less useful to the navigator, from the assistance they give him in finding the longitude at sea. For a long time, notwithstanding the perfection of finish and adjustment bestowed upon clocks and watches, an apparently insurmountable obstacle presented itself to their uniform and regular movement; this obstacle was the change of dimensions to which the regulating parts of the machine were subject by alterations of temperature. A clock may be defined as an instrument for registering the number of beats made by a pendulum: now the time of oscillation of a pendulum depends *principally* upon its length; any alteration in this condition will seriously affect the rate of the clock. The material of which the rod of the pendulum is composed is subject to expansion and contraction by changes of temperature; so that a pendulum adjusted to vibrate seconds at 60° (15°·5C) would go too slow when the temperature rose to 70° (21°·1C), from its elongation, and too fast when the temperature fell to 50° (10°C), from the opposite cause.

Fig. 24.

This great difficulty has been overcome; by making the rod of a number of bars of iron and brass, or iron and zinc, metals whose rates of expansion are different, and arranging these bars in such a manner that the expansion in one direction of the iron shall be exactly compensated by that in the opposite direction of the brass or zinc, it is possible to maintain under all circumstances of temperature an invariable distance between the points of suspension and of oscillation. This is often called the *gridiron*

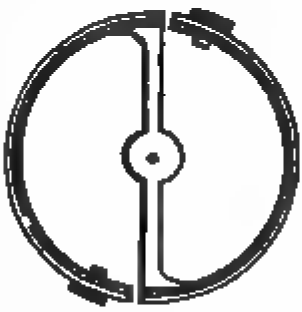
pendulum; fig. 24 will clearly illustrate its principle; the shaded bars are supposed to be iron and the others brass.

Fig. 25.

A still simpler compensation pendulum (fig. 25) is thus constructed. The weight or bob, instead of being made of a disc of metal, consists of a cylindrical glass jar containing mercury, which is held by a stirrup at the extremity of the steel pendulum-rod. The same increase of temperature which lengthens this rod, causes the volume of the mercury to enlarge, and its level to rise in the jar; the centre of gravity is thus elevated, and by properly adjusting the quantity of mercury in the glass, the virtual length of the pendulum may be made constant.

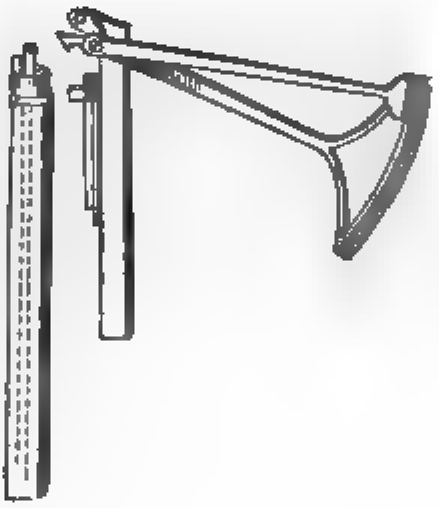
In watches, the governing power is a horizontal weighted wheel, set in motion in one direction by the machine itself, and in the other by a fine spiral spring. The rate of going depends greatly on the diameter of this wheel, and the diameter is of necessity subject to variation by change of temperature. To remedy the evil thus involved, the circumference of the balance-wheel is made of two metals having different rates of expansion, fast soldered together, the most expansible being on the outside. The compound rim is also cut through in two or more places, as represented in fig. 26. When the watch is exposed to a high temperature, and the diameter of the wheel becomes enlarged by expansion, each segment is made, by the same agency, to assume a sharper curve, whereby its centre of gravity is thrown inwards, and the expansive effect completely compensated. Many other beautiful applications of the same principle might be pointed out; the metallic thermometer of M. Bréguet is one of these.

Fig. 26.



Mr. Daniell very skilfully applied the expansion of a rod of metal to the measurement of temperatures above those capable of being taken by the thermometer. A rod of iron or platinum, about five inches long, is dropped into a tube of black-lead ware; a little cylinder of baked porcelain is put over it, and secured in its place by a platinum strap and a wedge of porcelain. When the whole is exposed to heat, the expansion of the bar drives forward the cylinder, which moves with a certain degree of friction, and shows, by the extent of its displacement, the lengthening which the bar had undergone. It remains, therefore, to measure the amount of this displacement, which must be very small, even when the heat has been exceedingly intense. This is effected by the contrivance shown in fig. 27, in which the motion of the longer arm of the lever carrying the vernier of the scale is multipled by 10, in consequence of its superior length. The scale itself is made comparable with that of the ordinary thermometer, by plunging the instrument into a bath of mercury near its point of congelation, and afterwards into another of the same metal in a boiling state, and marking off the interval. By this instrument the melting-point

Fig. 27.



of cast iron was fixed at 2786° Fahrenheit (1530°C), and the greatest heat of a good wind-furnace at about 3300° (1815°C).

The actual amount of expansion which different solids undergo by the same increase of heat, has been carefully investigated. The following are some of the results obtained by MM. Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by rods of the undermentioned bodies in passing from 32° (0°C) to 212° (100°C).

English flint glass	$\frac{1}{1248}$	Soft iron	$\frac{1}{819}$
Common French glass	$\frac{1}{1147}$	Gold	$\frac{1}{682}$
Glass without lead	$\frac{1}{1142}$	Copper	$\frac{1}{584}$
Another specimen	$\frac{1}{1090}$	Brass	$\frac{1}{533}$
Steel untempered	$\frac{1}{927}$	Silver	$\frac{1}{524}$
Tempered steel	$\frac{1}{807}$	Lead	$\frac{1}{351}$

From the *linear* expansion, the *cubic* expansion (or increase of volume) may be easily calculated. When an approximation only is wanted, it will be sufficient to triple the fraction expressing the increase in one dimension.

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated, but above the boiling-point of water the rate of expansion becomes irregular and more rapid.

The force exerted in the act of expansion is very great; in laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

A very useful little application of expansion by heat is that to the cutting of glass by a hot iron; this is constantly practised in the laboratory for a great variety of purposes. The glass to be cut is marked with ink in the wished-for direction, and then a crack commenced by any convenient method, at some distance from the desired line of fracture, may be led by the point of a heated iron rod along the latter with the greatest precision.

Expansion of Fluids.—The dilatation of a fluid may be determined by filling with it a thermometer, in which the relation between the capacity of the ball and that of the stem is exactly known, and observing the height of the column at different temperatures. It is necessary in this experiment to take into account the effects of the expansion of the glass itself, the observed result being evidently the *difference* of the two.

Liquids vary exceedingly in this particular. The following table is taken from Péclet's *Elémens de Physique.*

Apparent Dilatation in Glass between 32° (0°C) *and* 212° (100°C).

Water	$\frac{1}{23}$
Hydrochloric acid, sp. gr. 1·137	$\frac{1}{27}$
Nitric acid, sp. gr. 1·4	$\frac{1}{9}$
Sulphuric acid, sp. gr. 1·85	$\frac{1}{17}$
Ether	$\frac{1}{14}$
Olive oil	$\frac{1}{12}$
Alcohol	$\frac{1}{9}$
Mercury	$\frac{1}{64}$

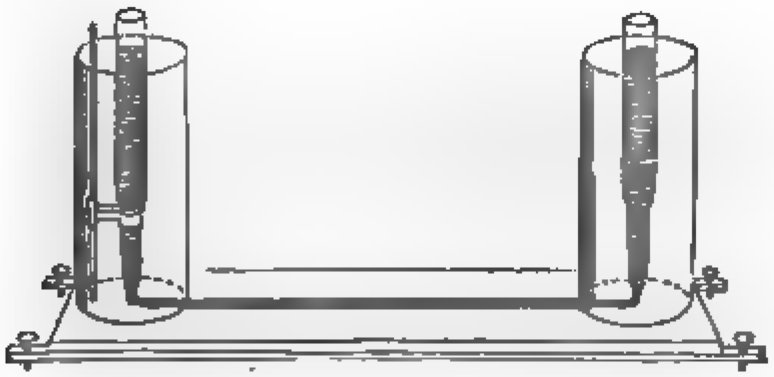
Most of these numbers must be taken as representing mean results. For there are few fluids which, like mercury, expand regularly between these temperatures. Even mercury above 212° (100°C) expands irregularly, as the following table shows.

Absolute Expansion of Mercury for 180°.

Between 32° (0°C) and 212° (100°C)	$\frac{1}{55 \cdot 5}$
Between 212° (100°C) and 392° (200°C)	$\frac{1}{54 \cdot 25}$
Between 392° (200°C) and 572° (300°C)	$\frac{1}{53}$

The absolute amount of expansion of mercury is, for many reasons, a point of great importance; it has been very carefully determined by a method independent of the expansion of the containing vessel. The apparatus employed for this purpose by MM. Dulong and Petit is shown in fig. 28, divested, however, of many of its subordinate parts. It consists of two upright glass tubes, connected at their bases by a horizontal tube of much smaller dimensions. Since a free communication exists between the two tubes, mercury poured into the one will rise to the same level in the other, provided its temperature is the same in both tubes; when this is not the case, the hottest column will be the tallest, because the expansion of the metal diminishes its specific-gravity, and the law of hydrostatic equilibrium requires that the heights of such columns should be inversely as their densities. By the aid of the outer cylinders, one of the tubes is maintained constantly at 32° (0°C), while the other is raised, by means of heated water or oil, to any required temperature. The perpendicular heights of the columns may then be read off by a horizontal micrometer telescope, moving on a vertical divided scale.

Fig. 28.



These heights represent volumes of equal weight, because volumes of equal weight bear an inverse proportion to the densities of the liquids, so that the amount of expansion admits of being very easily calculated. Thus, let the column at 32° (0°C) be 6 inches high, and that at 212° (100°C) 6·108 inches, the increase of height, 108 on 6,000, or $\frac{1}{55 \cdot 5}$ part of the whole, must represent the absolute cubical expansion.

The indications of the mercurial thermometer are inaccurate when very high ranges of temperature are concerned, from the increased expansibility of the metal; on this account, a certain correction is necessary in many experiments, and tables for this purpose have been drawn up.[1]

An exception to the regularity of expansion in fluids, exists in the case of water; it is so remarkable, and its consequences so important, that it is necessary to advert to it particularly.

Let a large thermometer-tube be filled with water at the common tempe-

[1] *Below 400° Fahrenheit (204°·4C)* the error may be neglected; at 500° (260°C) it is about *2°; at 630° (332°·2C) 6°.—Regnault.*

rature of the air, and then artificially cooled. The liquid will be observed to contract regularly, until the temperature falls to about 40° (4°·4C), or 8° above the freezing-point. After this, a farther reduction of temperature causes expansion instead of contraction in the volume of the water, and this expansion continues until the liquid arrives at its point of congelation, when so sudden and violent an enlargement takes place, that the vessel is almost invariably broken. At the temperature of 40° (4°·4C), or more correctly, perhaps, 39°·5 (4°·1C), water is at its maximum density; increase or diminution of heat produces upon it, for a short time, the same effect.

A beautiful experiment of Dr. Hope illustrates the same fact. If a tall jar filled with water at 50° (10°C) or 60° (15°·5C) and having in it two small thermometers, one at the bottom and the other near the surface, be placed at rest in a very cold room, the following changes will be observed. The thermometer at the bottom will fall more rapidly than that at the top, until it has attained the temperature of 40° (4°·4C) after which it will remain stationary. At length the upper thermometer will also mark 40° (4°·4C) but still continue to sink as rapidly as before, while that at the bottom remains stationary. It is easy to explain these effects: the water in the upper part of the jar is rapidly cooled by contact with the air; it becomes denser in consequence, and falls to the bottom, its place being supplied by the lighter and warmer liquid, which in its turn suffers the same change; and this circulation goes on until the whole mass of water has acquired its condition of maximum density, that is, until the temperature has fallen to 40° (4°·4C). Beyond this, loss of heat occasions expansion instead of contraction, so that the very cold water on the surface has no tendency to sink, but rather the reverse.

This singular anomaly in the behaviour of water is attended by the most beneficial consequences, in shielding the inhabitants of the waters from excessive cold. The deep lakes of the North American Continent never freeze, the intense and prolonged cold of the winters of those regions being insufficient to reduce the temperature of such masses of water to 40° (4°·4C). Ice, however, of great thickness forms over the shallow portions, and the rivers, and accumulates in mounds upon the beaches, where the waves are driven up by the winds.

Sea-water has a maximum density at the same temperature as fresh water. The depths of the Polar Seas exhibit this temperature throughout the year, while the surface-water is in summer much above, and in winter much below, 40° (4°·4C); in both cases being specifically lighter than water at that temperature. This gradual expansion of water cooled below 40° (4°·4C) must be carefully distinguished from the great and sudden increase of volume it exhibits in the act of freezing, and in which respect it resembles many other bodies which expand on solidifying. It may be observed that the force thus exerted by freezing water is enormous. Thick iron shells quite filled with water, and exposed with their fuse-holes securely plugged, to the cold of a Canadian winter night, have been found the following morning split in fragments. The freezing of water in the joints and crevices of rocks is a most potent agent in their disintegration.

Expansion of Gases.—This is a point of great practical importance to the chemist, and happily we have very excellent evidence upon the subject. The following four propositions exhibit, at a single view, the principal facts of the case:—

1. All gases expand alike for equal increments of heat; and all vapours, when remote from their condensing-points, follow the same law.
2. The rate of expansion is not altered by a change in the state of *compression*, or elastic force of the gas itself.

3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to $\frac{1}{480}$ part of the volume of the gas at 0° Fahrenheit, for each degree of the same scale.[1]

It will be unnecessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's *Elémens de Physique*, and in the papers of MM. Magnus[2] and Regnault[3] all the information he may require.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume which 100 cubic inches of any gas at 50° (10°C) would become on the temperature rising to 60° (15°·5C).

The rate of expansion is $\frac{1}{460}$ of the volume at 0° for each degree; or 460 measures at 0° become 461 at 1°, 462 at 2°, ·· 460 + 50 = 510 at 50°, and 460 + 60 = 520 at 60°. Hence

Meas. at 50°.		Meas. at 60°.		Meas. at 50°.		Meas. at 60°.
510	:	520	=	100	:	101·96.

If this calculation is required to be made on the centigrade scale, it must be remembered that the zero of that scale is the melting point of ice. Above this temperature the expansion for each degree of the centigrade scale is $\frac{1}{273}$ of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

Note.—Of the four propositions stated in the text, the first and second have quite recently been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experiments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small, that for most purposes it may with perfect safety be neglected. Neither is the state of elasticity altogether indifferent, the expansion being sensibly *greater* for an equal rise of temperature when the gas is in a compressed state.

It is important to notice, that the greatest deviations from the rule are exhibited by those gases which, as will hereafter be seen, are most easily liquefied, such as carbonic acid, cyanogen, and sulphurous acid, and that the discrepancies become smaller and smaller as the elastic force is lessened; so that, if means existed for comparing the different gases in states *equally distant* from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of MM. Dulong and Petit give for the rate of expansion $\frac{1}{448}$ of the volume at 0°: this is no doubt too high. Those of Rudburg give $\frac{1}{481}$; of Magnus $\frac{1}{459}$; and of Regnault $\frac{1}{458}$: the fraction $\frac{1}{460}$ is adopted in the test as a convenient number, sufficiently near the mean of the three preceding, to answer all purposes.

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[1] Or the amount of expansion is equal to 1-492d part of the volume the gas occupies at 32°F. for each degree of Fahrenheit's scale. On the centigrade scale the expansion is 1-273d part of the bulk at 0°C.—R. B.

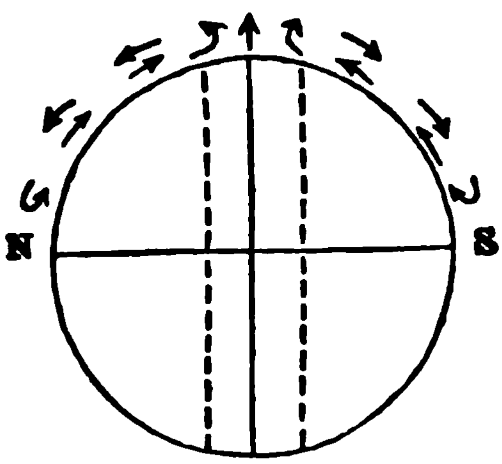
[2] *Poggendorff's Annalen*, iv. 1.

[3] Ann. Chim. et Phys., 3rd series, iv 5. and v. 52.

The ready expansibility of air by heat gives rise to the phenomena of winds. In the temperate regions of the earth these are very variable and uncertain, but within and near the tropics a much greater regularity prevails; of this the *trade-winds* furnish a beautiful example.

The smaller degree of obliquity with which the sun's rays fall in the localities mentioned, occasions the broad belt thus stretching round the earth to become more heated than any other part of the surface. The heat thus acquired by absorption is imparted to the lowest stratum of air, which, becoming expanded, rises, and gives place to another, and in this manner an ascending current is established,—the colder and heavier air streaming in laterally from the more temperate regions, north and south, to supply the partial vacuum thus occasioned. A circulation so commenced will be completed in obedience to the laws of hydrostatics, by the establishment of counter-currents in the higher parts of the atmosphere, having directions the reverse of those on the surface. (Fig. 29.)

Fig. 29.

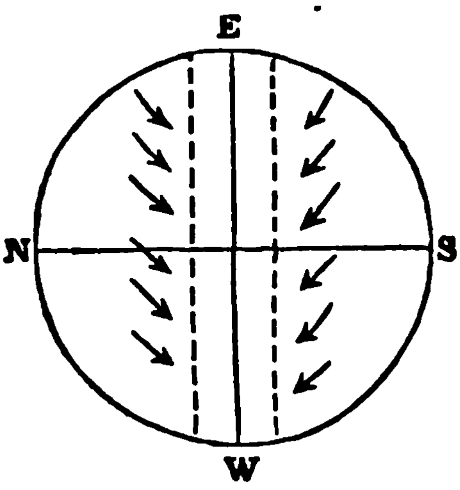


Such is the effect produced by the unequal heating of the equatorial parts, or, more correctly, such would be the effect were it not greatly modified by the earth's movement of rotation.

As the circumference of the earth is, in round numbers, about 24,000 miles, and since it rotates on its axis, from west to east, once in 24 hours, the equatorial parts must have a motion of 1000 miles per hour; this velocity diminishes rapidly towards each pole, where it is reduced to nothing.

The earth in its rotation carries with it the atmosphere, whose velocity of movement corresponds, in the absence of disturbing causes, with that part of the surface immediately below it. The air which rushes towards the equator, to supply the place of that raised aloft by its diminished density, brings with it the degree of momentum belonging to that portion of the earth's surface from which it set out, and as this momentum is less than that of the earth, under its new position, the earth itself travels faster than the air immediately over it, thus producing the effect of a wind blowing in a contrary direction to that of its own motion. The original north and south winds are thus deviated from their primitive directions, and made to blow more or less from the eastward, so that the combined effects of the unequal heating and of the movement of rotation is to generate in the northern hemisphere a constant north-east wind, and in the southern hemisphere an equally constant south-east wind. (Fig. 30.)

Fig. 30.



In the same manner the upper or return current is subject to a change of direction in the reverse order; the rapidly-moving wind of the tropics, transferred laterally towards the poles, is soon found to travel faster than the earth beneath it, producing the effect of a westerly wind, which modifies the primary current.

The regularity of the trade-winds is much interfered with by the neighbourhood of large continents, which produce local effects upon a scale sufficiently great to modify deeply the direction and force of the wind. This is the case in the Indian Ocean. They usually extend from about the 28th

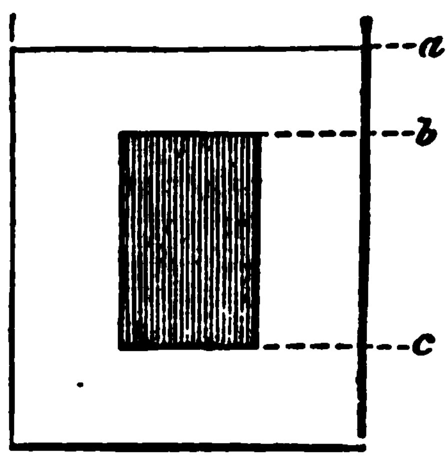
degree of latitude in both hemispheres, to within 8° of the equator, but are subject to some variations in this respect. Between them, and also beyond their boundaries, lie belts of calms and light variable winds, and beyond these latter, extending into higher latitudes in both hemispheres, westerly winds usually prevail. The general direction of the trade-wind of the Northern hemisphere is E.N.E., and that of the Southern hemisphere E.S.E.

The trade-winds, it may be remarked, furnish an admirable physical proof of the reality of the earth's movement of rotation.

The theory of the action of chimneys, and of natural and artificial ventilation, belongs to the same subject.

Let the reader turn to the demonstration given of the Archimedean hydrostatic theorem; let him once more imagine a body immersed in water, and having a density equal to that of the water; it will remain in equilibrium in any part beneath the surface, and for these reasons:—The force which presses it downwards is the weight of the body added to the weight of the column of water above it; the force which presses it upwards is the weight of a column of water equal to the height of both conjoined;—the density of the body is that of water, that is, it weighs as much as an equal bulk of that liquid; consequently, the downward and upward forces are equally balanced, and the body remains at rest.

Fig. 31.



Next, let the circumstances be altered; let the body be lighter than an equal bulk of water; the pressure upwards of the column of water, *a c*, fig. 31, is no longer compensated by the downward pressure of the corresponding column of solid and water above it; the former force preponderates, and the body is driven upwards. If, on the contrary, the body be specifically heavier than the water, then the latter force has the ascendancy, and the body sinks.

All things so described exist in a common chimney; the solid body, of the same density as that of the fluid in which it floats, is represented by the air in the chimney-funnel; the space *a b* represents the whole atmosphere above it. When the air inside and outside the chimney is at the same temperature, equilibrium takes place, because the downward tendency of the air within is counteracted by the upward pressure of that without.

Now, let the chimney be heated; the air suffers expansion, and a portion is expelled; the chimney therefore contains a smaller weight of air than it did before; the external and internal columns no longer balance each other, and the warmer and lighter air is forced upwards from below, and its place supplied by cold air. If the brick-work, or other material of which the chimney is constructed, retain its temperature, this second portion of air is disposed of like the first, and the ascending current continues, so long as the sides of the chimney are hotter than the surrounding air.

Sometimes, owing to sudden changes of temperature in the atmosphere, the chimney may happen to be colder than the air about it. The column within forthwith suffers contraction of volume; the deficiency is filled up from without, and the column becomes heavier than one of similar height on the outside; the result is, that it falls out of the chimney, just as the heavy body sinks in the water, and has its place occupied by air from above. A descending current is thus produced, which may be often noticed in summer time by the smoke from neighbouring chimneys finding its way into rooms which have been, for a considerable period, without fire.

The ventilation of mines has long been conducted upon the same principle

and more recently it has been applied to dwelling-houses and assembly-rooms. The mine is furnished with two shafts, or with one shaft, divided throughout by a diaphragm of boards; and these are so arranged, that air forced down the one shall traverse the whole extent of the workings before it escapes by the other. A fire kept up in one of these shafts, by rarefying the air within, and causing an ascending current, occasions fresh air to traverse every part of the mine, and sweep before it the noxious gases, but too frequently present.

CONDUCTION OF HEAT.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron and the other of glass, be held in the flame of a spirit-lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity within an inch of the red-hot portion.

Experiments made by analogous, but more accurate methods, have established a numerical comparison of the conducting powers of many bodies; the following may be taken as a specimen :—

Gold	1000	Tin	304
Silver	973	Lead	179
Copper	898	Marble	23·6
Iron	374	Porcelain	12·2
Zinc	363	Fire-clay	11·4

As a class, the metals are by very far the best conductors, although much difference exists between them; stones, dense woods, and charcoal, follow next in order; then liquids in general, and gases, whose conducting power is almost inappreciable.

Under favourable circumstances, nevertheless, both liquids and gases may become rapidly heated; heat applied to the bottom of the containing vessel is very speedily communicated to its contents; this, however, is not so much by conduction as by convection, or carrying. A complete circulation is set up; the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident, and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories, and in chemical works a serpentine metal tube containing hot oil is often used for heating stills and evaporating pans; the two extremities of the tube are connected with the ends of another spiral built into a small furnace at a lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

CHANGE OF STATE.

If equal weights of water at 32° (0°C) and water at 174° (78°·8C) be mixed, the temperature of the mixture will be the mean of the two temperatures, or 103° (39°·4C). If the same experiment be repeated with snow, or finely powdered ice, at 32° (0°C) and water at 174° (78° 8C), the temperature of the whole will be still only 32° (0°C), *but the ice will have been melted*

$$\left.\begin{array}{l}\text{1 lb. of water at } 32^\circ\ (0^\circ C) \\ \text{1 lb. of water at } 174^\circ\ (78^\circ\cdot 8C)\end{array}\right\} = \text{2 lb. water at } 103^\circ\ (39^\circ\cdot 4C)$$

$$\left.\begin{array}{l}\text{1 lb. of ice at } 32^\circ\ (0^\circ C) \\ \text{1 lb. of water at } 174^\circ\ (78^\circ\cdot 8C)\end{array}\right\} = \text{2 lb. water at } 32^\circ\ (0^\circ C)$$

In the last experiment, therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 142° (78°·8C).

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called latent heat, or, better, head of fluidity.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a pound of water placed over it would have its temperature raised 10° (5°·5C) per minute. Starting with water at 32° (0°C), in rather more than 14 minutes its temperature would have risen 142° (78°·8); but the same quantity of ice at 32° (0°C), exposed for the same interval of time, would not have its temperature raised a single degree. But, then, it would have become water; the heat received would have been exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced 10° or more below its freezing-point without the formation of ice; but then, if a little agitation be communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to 32° (0°C); the heat disengaged by the freezing of a small portion of the water will have been sufficient to raise the whole contents of the jar 10° (5°·5C).

This curious condition of instable equilibrium shown by the very cold water in the preceding experiment, may be reproduced with a variety of solutions which tend to crystallize or solidify, but in which that change is for a while suspended. Thus, a solution of crystallized sulphate of soda in its own weight of warm water, left to cool in an open vessel, deposits a large quantity of the salt in crystals. If the warm solution, however, be filtered into a clean flask, which when full is securely corked and set aside to cool undisturbed, no crystals will be deposited, even after many days, until the cork is withdrawn and the contents of the flask violently shaken. Crystallization then rapidly takes place in a very beautiful manner, and the whole becomes perceptibly warm.

The law thus illustrated in the case of water is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes a solid, heat to a corresponding extent is given out. The amount of latent heat varies much with different substances, as will be seen by the table: —

Water[1] . . .	142°	(78°·8C)	Zinc . . .	493°	(273°·8C)
Sulphur . . .	145	(80 ·5C)	Tin . . .	500	(277 ·7C)
Lead . . .	162	(90 ·5C)	Bismuth . .	550	(305 ·5C)

When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of the many frigorific mixtures to be found described in some of the older chemical treatises. When snow or powdered ice is mixed with common salt, and a thermometer is plunged into the mass, the mercury sinks to 0° (—17°·7C), while the whole, after a short period, becomes fluid by the attraction between the water and the salt; such a mixture is very often used

[1] MM. De la Provostaye and Regnault, Ann. Chim. et Phys., 3d series, viii. 1.

in chemical experiments to cool receivers and condense the vapours of volatile liquids. Powdered crystallized chloride of calcium and snow produce cold enough to freeze mercury. Even powdered nitrate of potassa, or sal-ammoniac, dissolved in water, occasions a very notable depression of temperature; in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation is to be traced between the actual melting-point of a substance, and its latent heat when in a fused state.

A law of exactly the same kind as that described affects universally the gaseous condition; change of state from solid or liquid to gas is accompanied by absorption of sensible heat, and the reverse by its disengagement. The latent heat of steam and other vapours may be ascertained by a similar mode of investigation to that employd in the case of water.

When water at 32° (0°C) is mixed with an equal weight of water at 212° (100°C), the whole is found to possess the mean of the two temperatures, or 122° (50°C); on the other hand, 1 part by weight of *steam* at 212° (100°C) when condensed into cold water, is found to be capable of raising 5·6 parts of the latter from the freezing to the boiling-point, or through a range of 180° (100°C). Now 180 × 5·6 = 1008; that is to say, steam at 212° (100°C) in becoming water at 212°, parts with enough heat to raise a weight of water equal to its own (if it were possible) 1008° (560°C) of the thermometer. When water passes into steam, the same quantity of sensible heat becomes latent.

The vapours of other liquids seem to have less latent heat than that of water; the following table is by Dr. Ure, and serves well to illustrate this point:—

Vapour of	water	967°	(537°·2C)
"	alcohol	442	(246 ·6C)
"	ether	302	(167 ·7C)
"	petroleum	178	(98 ·8C)
"	oil of turpentine	178	(98 ·8C)
"	nitric acid	532	(295 ·5C)
"	liquor ammoniæ	837	(145 ·0C)
"	vinegar	875	(486 ·1C)

Ebullition is occasioned by the formation of bubbles of vapour within the body of the evaporating liquid, which rise to the surface like bubbles of permanent gas. This occurs in different liquids at very different temperatures; under the same circumstances, the boiling-point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration:—

Substance.	Boiling-point.	
Ether	96°	(35°·5C)
Bisulphide of carbon	115	(46 ·1C)
Alcohol	177	(80 ·5C)
Water	212	(100 C)
Nitric acid, strong	248	(120 C)
Oil of turpentine	312	(155 ·5C)
Sulphuric acid	620	(326 ·2C)
Mercury	662	(350 C)

For ebullition to take place, it is necessary that the elasticity of the vapour should be able to overcome the cohesion of the liquid and the pressure upon its surface; hence the extent to which the boiling-point may be modified.

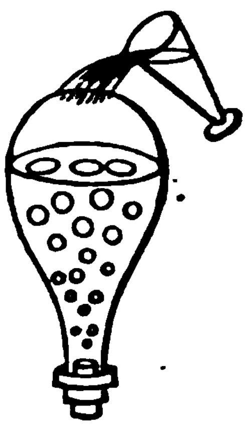
Water, under the usual pressure of the atmosphere, boils at 212° (100°C);

in a partially exhausted receiver or on a mountain-top it boils at a much lower temperature; and in the best vacuum of an excellent air-pump, over oil of vitriol, which absorbs the vapour, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapour to an almost unlimited extent; a temperature of 350° (177°C) or 400° (204°C) is very easily obtained; and, in fact, it is said that it may be made red-hot, and yet retain its fluidity.

There is a very simple and beautiful experiment illustrative of the effect of diminished pressure in depressing the boiling point of a liquid. A little water is made to boil for a few minutes in a flask or retort (fig. 32) placed over a lamp, until the air has been chased out, and the steam issues freely from the neck. A tightly fitting cork is then inserted, and the lamp at the same moment withdrawn. When the ebullition ceases it may be renewed at pleasure for a considerable time by the affusion of cold water, which, by condensing the vapour within, occasions a partial vacuum.

Fig. 32.



The nature of the vessel, or rather, the state of its surface, exercises an influence upon the boiling-point, and this to a much greater extent than was formerly supposed. It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but it has lately been shown[1] that by particular management a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first will boil at 211° (99°·4C), while in the second it will often rise to 221° (105°C) or even higher; a momentary burst of vapour then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapour, while the temperature sinks to 212° (100°C), and there remains stationary. These remarkable effects must be attributed to an attraction between the surface of the vessel and the liquid.[2]

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[1] Marcet, Ann. Chim. et Phys., 3d series, v. 449.

[2] A remarkable modification of the relation between the temperature of liquids and the vessel containing them, results where the repulsive action predominates. When a small quantity of water is thrown into a red-hot platinum crucible, it assumes a spheroidal form, presents no appearance of ebullition, but only a rotary motion, and evaporates very slowly; but when the temperature falls to 300°, this spheroidal condition is lost, the liquid boils and is soon dissipated. In the spheroidal state there is no contact between the water and metal, in consequence of the high tension of the small quantity of vapour which is formed and surrounds the globule, but on the fall in temperature, the tension lessens and with it the repulsive action, contact takes place and the heat is rapidly communicated to the liquid, which at once is converted into steam. So slight is the influence of the caloric of the vessel on the contained liquid in this condition, that if liquid sulphurous acid be poured on the globule, the water is by the sudden evaporation of the acid converted into ice at the bottom of the red-hot crucible. When a liquid which boils at a low temperature, is thrown on another heated nearly to ebullition and whose boiling-point is high, the spheroidal state is likewise assumed, as water on oil, spirits of turpentine, sulphuric acid, &c., and ether on water, &c.

As connected with this phenomenon, it has been observed that perfect immunity from the caloric of highly heated liquids may be obtained by previously moistening the part to which the application is made with some fluid which evaporates at a low temperature. Thus the hand, while moistened with ether, may be plunged into boiling-water without even the sensation of heat. When wet with water it may be dipped into melted lead without injury or strong sensation of heat, and still less is perceived if alcohol or ether be used. A similar experiment has been performed with melted cast-iron as it runs from the furnace, and the

A cubic inch of water in becoming steam under the ordinary pressure of the atmosphere expands into 1696 cubic inches, or nearly a cubic foot.

Steam, *not in contact with water*, is affected by heat in precisely the same manner as the permanent gases; its rate of expansion and increase of elastic force are the same. When water is present, however, this is no longer the case, but on the contrary, the elastic force increases in a far more rapid proportion.

This elastic force of steam in contact with water, at different temperatures, has been very carefully determined by MM. Arago and Dulong, and very lately by M. Regnault. The force is expressed in atmospheres; the absolute pressure upon any given surface can be easily calculated, allowing 14·6 lb. to each atmosphere. The experiments were carried to twenty-five atmospheres, at which point the difficulties and danger became so great as to put a stop to the inquiry: the rest of the table is the result of calculations founded on the data so obtained.

Pressure of steam in atmospheres.	Corresponding temperature. F.	C.	Pressure of steam in atmospheres.	Corresponding temperature. F.	C.
1	212°	100°	13	381°	194°
1·5	234	112 ·2	14	387	197 ·7
2	251	121 ·2	15	393	200 ·5
2·5	264	128 ·8	16	398	203 ·1
3	275	135	17	404	206 ·2
3·5	285	140 ·5	18	409	209 ·4
4	294	145 ·5	19	414	212 ·2
4·5	300	148 ·8	20	418	214 ·4
5	308	153 ·1	21	423	217 ·2
5·5	314	156 ·2	22	427	219 ·4
6	320	160	23	431	221 ·2
6·5	326	163 ·1	24	436	224 ·4
7	332	166 ·2	25	439	226 ·1
7·5	337	169 ·4	30	457	236 ·1
8	342	172 ·2	35	473	245 ·1
9	351	177 ·2	40	487	252 ·7
10	359	181 ·2	45	491	255
11	367	186 ·1	50	511	266 ·1
12	374	190			

It is a very remarkable fact, that the latent heat of steam diminishes as the temperature of the steam rises, so that equal weights of steam thrown into cold water exhibit nearly the same heating power, although the actual temperature of the one portion may be 212° (100°C), and that of the other 350° (176°·2C) or 400° (204°·4C). This also appears true with temperatures below the boiling-point; so that it seems, to evaporate a given quantity of water the same *absolute* amount of heat is required, whether it be performed slowly at the temperature of the air, in a manner presently to be noticed, or whether it be boiled off under the pressure of twenty atmospheres. It is for this reason that the process of distillation in vacuo at a temperature which the hand can bear, so advantageous in other respects, can effect no *direct* saving in fuel.[1]

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dry parts subjected to the radiant caloric have been found more affected than that exposed to the melted metal.

The immunity in the case of using water as the moistening agent arises from the fact that the temperature of the globule in the spheroidal state is much below the boiling-point of the liquid.—R. B.

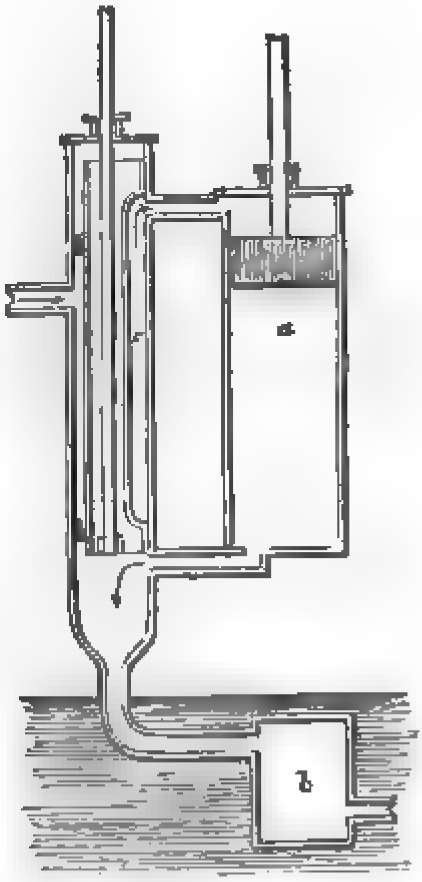
[1] The proposition in the text, of the sum of the latent and sensible heats of steam being a *constant quantity*, is known by the name of *Watt's law*, having been deduced by that illus-

economical applications of steam are numerous and extremely valu- they may be divided into two classes: those in which the heating is employed, and those in which its elastic force is brought into use. value of steam as a source of heat depends he facility with which it may be conveyed to points, and upon the large amount of latent contains, which is disengaged in the act of eation. An invariable temperature of 212°), or higher, may be kept up in the pipes or essels in which the steam is contained by penditure of a very small quantity of the Steam-baths of various forms are used in s with great convenience, and also by the ic chemist for drying filters and other ob- where excessive heat would be hurtful; a ood instrument of the kind was contrived Everitt. It is merely a small kettle (fig. rmounted by a double box or jacket, into the substance to be dried is put, and loosely covered by a card. The tus is placed over a lamp, and may be left without attention for many A little hole in the side of the jacket ent to the excess of steam.

Fig. 33.

principle of the steam-engine may ribed in a few words; its mechanical do not belong to the design of the volume. The machine consists es- y of a cylinder of metal, *a* (fig. 34), h works a closely-fitting solid piston, d of which passes, air-tight, through ing-box at the top of the cylinder, connected with the machinery to be motion, directly, or by the interven- an oscillating beam. A pipe commu- with the interior of the cylinder, and ith a vessel surrounded with cold called the condenser, marked *b* in the and into which a jet of cold water pleasure be introduced. A sliding- arrangement, shown at *c*, serves to communication between the boiler e cylinder, and the cylinder and the ser, in such a manner that while the is allowed to press with all its force ne side of the piston, the other, open condenser, is necessarily vacuous. lve is shifted by the engine itself at per moment, so that the piston is al- ly driven by the steam up and down a vacuum. A large air-pump, not in the engraving, is connected with the ser, and serves to remove any air that may enter the cylinder, and e water produced by condensation, together with that which may have jected.

Fig. 34.



is the vacuum or condensing steam-engine. In what is called the

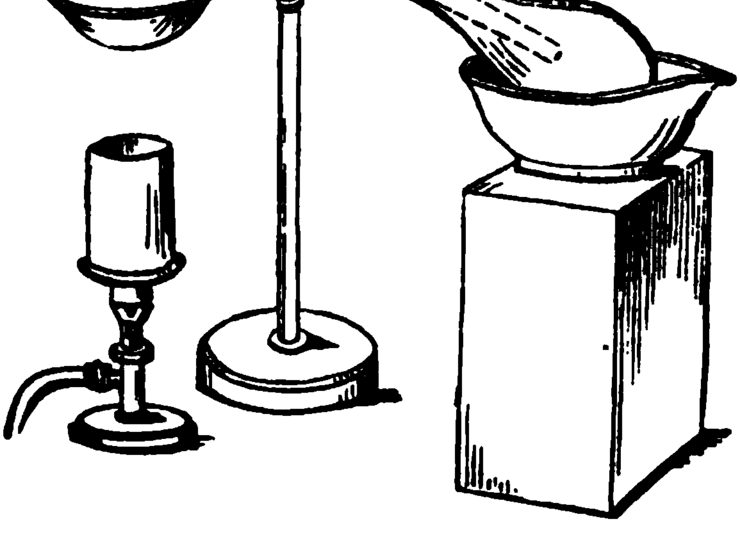
an from experiments of his own. It has always agreed well with the rough practi- tained by engineers, and has lately been confirmed to a great extent, although , by a series of elaborate experiments by M. Regnault.

high-pressure engine, the condenser and air-pump are suppressed, and the steam is allowed to escape at once from the cylinder into the atmosphere. It is obvious that in this arrangement the steam has to overcome the whole pressure of the air, and a much greater elastic force is required to produce the same effect; but this is to a very great extent compensated by the absence of the air-pump and the increased simplicity of the whole machine. Large engines, both on shore and in steam-ships, are usually constructed on the condensing principle, the pressure seldom exceeding six or seven pounds per square inch above that of the atmosphere; for small engines the high-pressure plan is, perhaps, preferable. Locomotive engines are of this kind.

A peculiar modification of the steam-engine, employed in Cornwall for draining the deep mines of that country, is now getting into use elsewhere for other purposes. In this machine economy of fuel is carried to a most extraordinary extent, engines having been known to perform the *duty* of raising more than 100,000,000 lb. of water one foot high by the consumption of a single bushel of coals. The engines are single-acting; the down-stroke, which is made against a vacuum, being the effective one, and employed to lift the enormous weight of the pump-rods in the shaft of the mine. When the piston reaches the bottom, the communication both with the boiler and the condenser is cut off, while an *equilibrium-valve* is opened, connecting the upper and lower extremities of the cylinder, whereupon the weight of the pump-rods draws the piston to the top and makes the up-stroke. The engine is worked *expansively*, as it is termed, steam of high tension being employed, which is cut off at one-eighth or even one-tenth of the stroke.

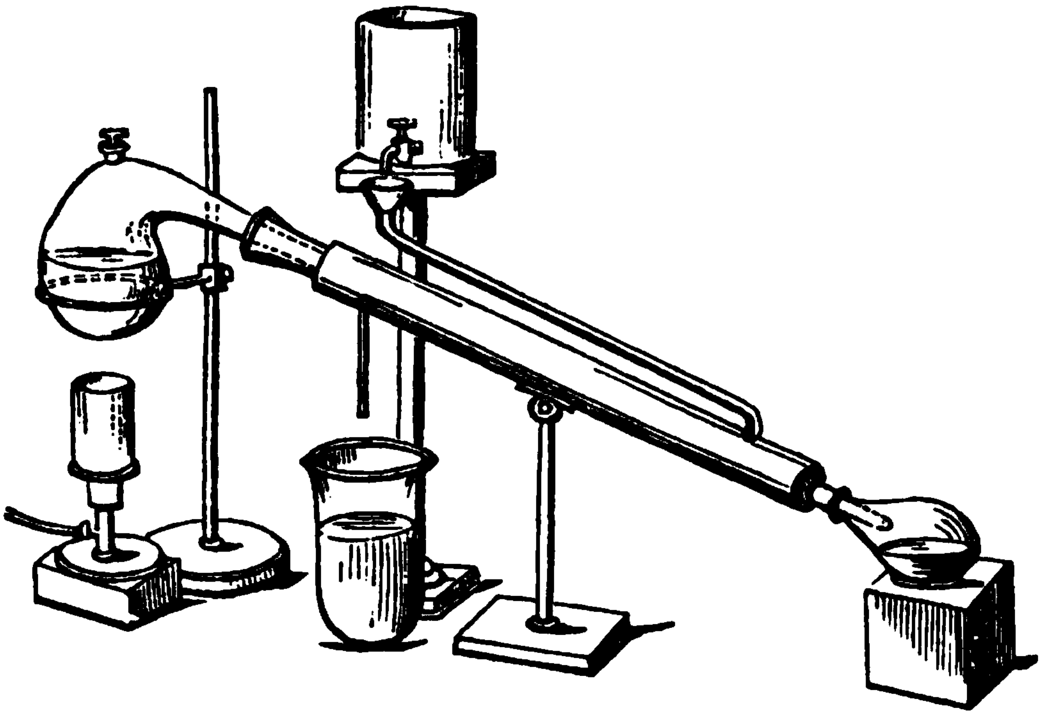
The process of distillation, which may now be noticed, is very simple; its object is either to separate substances which rise in vapour at different temperatures, or to part a volatile liquid from a substance incapable of volatilization. The same process applied to bodies which pass directly from the solid to the gaseous condition, and the reverse, is called *sublimation*. Every distillatory apparatus consists essentially of a boiler, in which the vapour is raised, and of a condenser, in which it returns to the liquid or solid condition. In the still employed for manufacturing purposes, the latter is usually a spiral metal tube immersed in a tub of water. The common retort and receiver constitute the simplest and most generally useful arrangement for distillation on the small scale; the retort is heated by a lamp or a char-

Fig. 35.



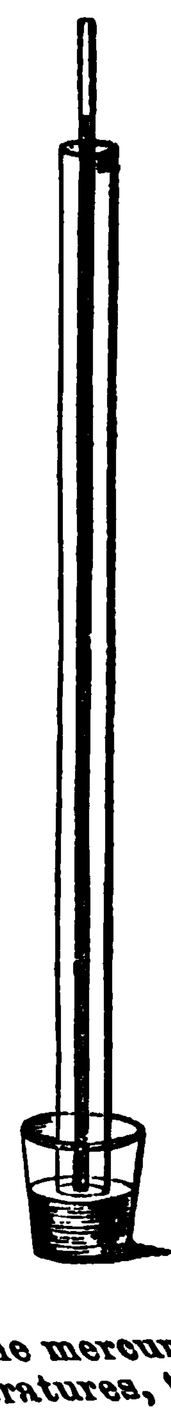
ire, and the receiver is kept cool, if necessary, by a wet cloth, or it may rrounded with ice. (Fig. 35.)

Fig. 36.



e condenser of Professor Liebig is a very valuable instru- in the laboratory; it consists of a glass tube (fig. 36), ing from end to end, fixed by perforated corks in the centre netal pipe, provided with tubes so arranged that a current d water may circulate through the apparatus. By putting pieces of ice into the little cistern, the temperature of this may be kept at 32° (0°C), and extremely volatile liquids nsed.

Fig. 37



uids evaporate at temperatures below their boiling-points; s case the evaporation takes place solely from the surface. r, or alcohol, exposed in an open vessel at the temperature air, gradually dries up and disappears; the more rapidly, armer and drier the air above it.

is fact was formerly explained by supposing that air and in general had the power of dissolving and holding in on certain quantities of liquids, and that this power in- ed with the temperature; such an idea is incorrect.

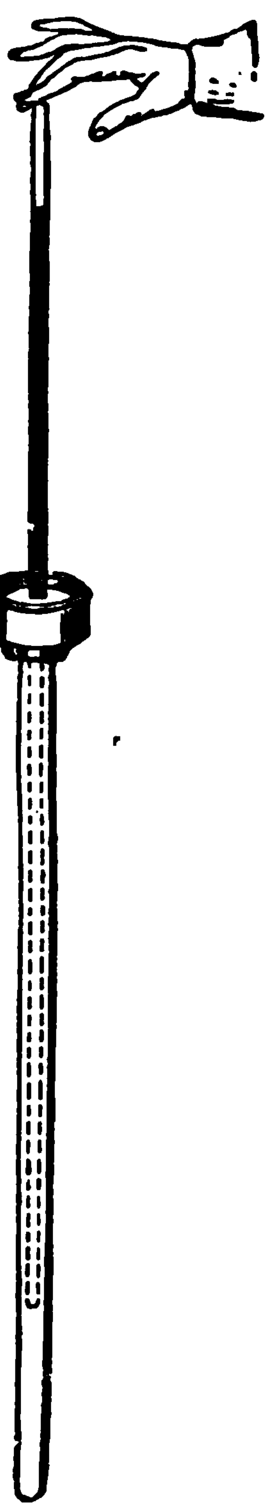
a barometer-tube (fig. 37) be carefully filled with mercury nverted in the usual manner, and then a few drops of water d up the tube into the vacuum above, a very remarkable will be observed; — the mercury will be depressed to a extent, and this depression will increase with increase of erature. Now, as the space above the mercury is void of nd the weight of the few drops of water quite inadequate count for this depression, it must of necessity be imputed e vapour which instantaneously rises from the water into acuum; and that this effect is really due to the elasticity nsion of the aqueous vapour, is easily proved by exposing arometer to a heat of 212° (100°C), when the depression e mercury will be complete, and it will stand at the same within and without the tube, indicating that at that temper- the elasticity of the vapour is equal to that of the atmo- e,—a fact which the phenomenon of ebullition has already n.

placing over the barometer a wide open tube dipping into the mercury , and then filling this tube with water at different temperatures, the

tension of the aqueous vapour for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter *down* one inch against the pressure of the atmosphere, would of course *elevate* a column of mercury to the same height against a vacuum, and in this way the tension may be very conveniently expressed. The following table was drawn up by Dr. Dalton, to whom we owe the method of investigation.

Temperature. F.	C.	Tension in inches of mercury.	Temperature. F.	C.	Tension in inches of mercury.
32°	0°	0·200	130°	54·4	4·34
40	4·4	0·263	140	60	5·74
50	10	0·375	150	65·5	7·42
60	15·5	0·524	160	71·1	9·46
70	21·1	0·721	170	76·6	12·13
80	26·6	1·000	180	82·2	15·15
90	32·2	1·360	190	87·7	19·00
100	37·7	1·860	200	93·3	23·64
110	43·3	2·530	212	100	30·00
120	48·8	3·330			

Fig. 38.



Other liquids tried in this manner are found to emit vapours of greater or less tension, for the same temperature, according to their different degrees of volatility: thus, a little ether introduced into the tube depresses the mercury 10 inches or more at the ordinary temperature of the air; oil of vitriol, on the other hand, does not emit any sensible quantity of vapour until a much greater heat is applied; and that given off by mercury itself in warm summer weather, although it may by very delicate means be detected, is far too little to exercise any effect upon the barometer. In the case of water, the evaporation is quite distinct and perceptible at the lowest temperatures, when frozen to solid ice in the barometer-tube; snow on the ground, or on a house-top, may often be noticed to vanish, from the same cause, day by day in the depth of winter, when melting was impossible.

There exists for each vapour a state of density which it cannot pass without losing its gaseous condition, and becoming liquid; this point is called the condition of maximum density. When a volatile liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the density of this vapour by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer (fig. 38), and the latter slowly sunk into a very deep cistern of mercury, it will be found that the height of the column of mercury in the tube above that in the cistern remains unaltered until the upper extremity of the barometer approaches the surface of the metal in the reservoir. It will be observed also, that, as the tube sinks, the little stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapour above it, and, consequently, no increase of density; for tension and density are always, under ordinary circumstances at least, directly proportionate to each other in the same vapour.

The point of maximum density of a vapour is dependent upon the temperature; it increases rapidly as the temperature rises. This is well shown in the case of water. Thus, taking the specific gravity of atmospheric air at 212° (100°C) = 1000, that of aqueous vapour in its greatest possible state of compression for the temperature will be as follows:—

Temperature. F.	C.	Specific gravity.	Weight of 100 cubic inches.
32°	0°	5·690	0·136 grains.
50	10·	10·293	0·247
60	15·5	14·108	0·338
100	37·7	46·500	1·113
150	65·5	170·293	4·076
212	100	625·000	14·962

The last number was experimentally found by M. Gay-Lussac; the others are calculated upon that by the aid of Dr. Dalton's table of tensions.

Thus, there are two distinct methods by which a vapour may be reduced to the liquid form; *pressure*, by causing increase of density until the point of maximum density for the particular temperature is reached; and *cold*, by which the point of maximum density is itself lowered. The most powerful effects are of course produced when both are conjoined.

For example, if 100 cubic inches of perfectly transparent and gaseous vapour of water at 100° (37°·7C), in the state above described, had its temperature reduced to 50° (10°C), not less than 0·87[1] grain of fluid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum; as much vapour rises, and the condition of maximum density is assumed in the same manner as if the space were perfectly empty; the sole difference lies in the length of time required. When a liquid evaporates into a vacuum, the point of greatest density is attained at once, while in the other case some time elapses before this happens; the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapour. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dry gas confined in a vessel closed by mercury, a little water is added, the latter immediately begins to evaporate, and after some time as much vapour will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapour will add itself to that of the gas, and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapour of water exists in the atmosphere at all times, and in all situations, and there plays a most important part in the economy of nature. The proportion of aqueous vapour present in the air is subject to great variation, and it often becomes exceedingly important to determine its quantity. This is easily done by the aid of the foregoing principles.

If the aqueous vapour be in its condition of greatest possible density for the temperature, or, as it is frequently, but most incorrectly expressed, the air be saturated with vapour of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapour of water be *below* its state of maximum density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point,

[1] 100 cubic inches aqueous vapours at 100° (37°·7C), weighing 1·113 grain, would at 50° (10°C), become reduced to 10·29 cubic inches, weighing 0·247 grain.

and it is determined with great facility by a very simple method. A little cup of thin tin-plate or silver, well polished, is filled with water at the temperature of the air, and a delicate thermometer inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac, until a deposition of moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

Suppose, by way of example, that the latter were 70° (21°·1C), and the dew-point 50° (10°C); the elasticity of the watery vapour present would correspond to a maximum density proper to 50° (10°C), and would support a column of mercury 0·375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29·625 inches would be supported by the pressure of the dry air, and the remaining 0·375 inch by the vapour. Now a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapour, occupying the same space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches of vapour at 70° (21°·1C), would become reduced by contraction, according to the usual law, to 1662·8 cubic inches at 50° (10°C): this vapour would be at its maximum density, having the specific gravity pointed out in the table; hence 1662·8 cubic inches would weigh 4·11 grains. The weight of the aqueous vapour contained in a cubic foot of air will thus be ascertained. In England the difference between the temperature of the air and the dew-point seldom reaches 30° (—1°·2C); but in the Deccan, with a temperature of 90° (32°·2C), the dew-point has been seen as low as 29° (—1°·6C) making the degree of dryness 61°.[1]

Another method of finding the proportion of moisture present in the air is to observe the rapidity with which evaporation takes place, and which is always in some relation to the degree of dryness. The bulb of a thermometer is covered with muslin, and kept wet with water, evaporation produces cold, as will presently be seen, and accordingly the thermometer soon sinks below the actual temperature of the air. When it comes to rest, the degree is noticed, and from a comparison of the two temperatures an approximation to the dew-point can be obtained by the aid of a mathematical formula contrived for the purpose. This is called the wet-bulb hygrometer; it is often made in the manner shown in fig. 30, where one thermometer serves to indicate the temperature of the air, and the other to show the rate of evaporation, being kept wet by the thread in connexion with the little water reservoir.

Fig. 30.

The perfect resemblance in every respect which vapours bear to permanent gases, led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid condition, and this surmise was, in the hands of Mr. Faraday, to a great extent verified. Out of the small number of such substances tried, not less than eight gave way; and it is quite fair to infer, that, had means of sufficient power been at hand, the rest would have shared the same fate, and proved to be nothing more than the vapours of volatile liquids in a state very far removed from that of their maximum density. The subjoined table represents the results of Mr. Faraday's first investigations,

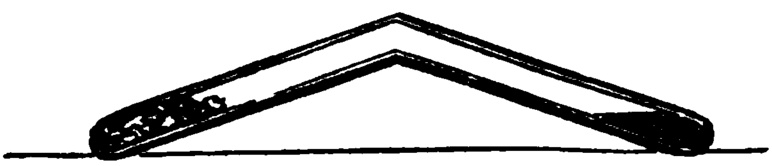
[1] Mr. Daniell, Introduction to Chemical Philosophy, p. 154.

with the pressure in atmospheres, and the temperature at which the condensation took place.[1]

	Atmospheres.	Temperature. F.	C.
Sulphurous acid	2	45°	7°·2
Sulphuretted hydrogen	17	50	10
Carbonic acid	36	32	0
Chlorine	4	60	15 ·5
Nitrous oxide	50	45	7 ·2
Cyanogen	3·6	45	7 ·2
Ammonia	6·5	50	10
Hydrochloric acid	40	50	10

The method of proceeding was very simple; the materials were sealed up in a strong narrow tube (fig. 40), together with a little pressure-gauge, con-

Fig. 40.



sisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by the application of heat, or otherwise, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the gauge.

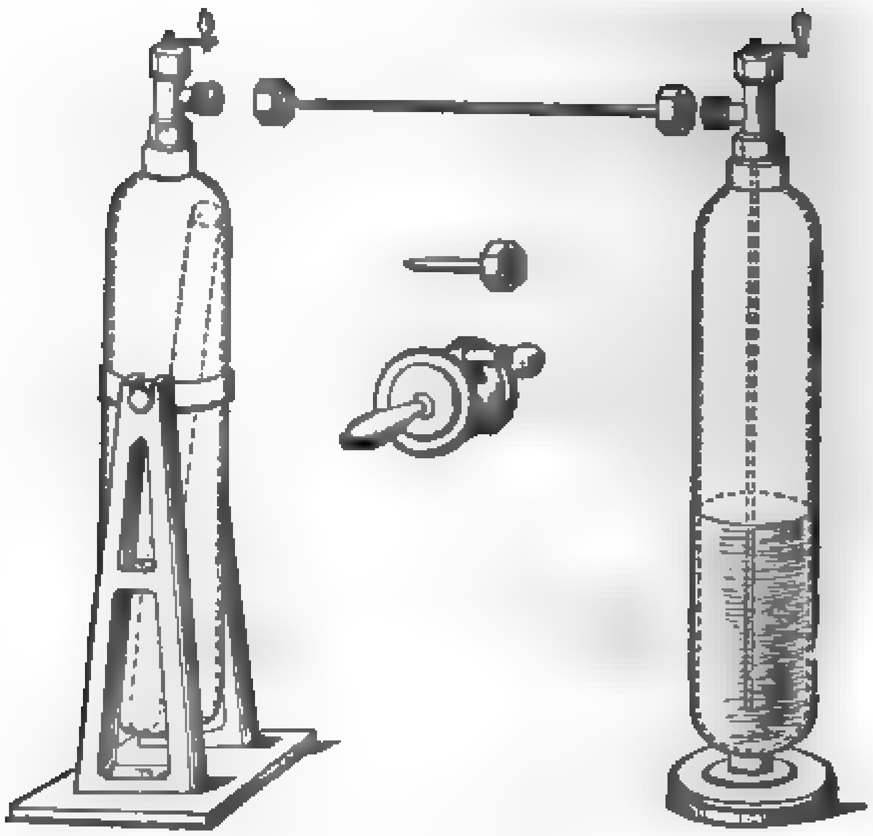
Mr. Faraday has since resumed, with the happiest results, the subject of the liquefaction of the permanent gases. By using narrow green glass tubes of great strength, powerful condensing syringes, and an extremely low temperature, produced by means to be presently described, olefiant gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron, were successively liquefied. Oxygen, hydrogen, nitrogen, nitric oxide, carbonic oxide, and coal-gas, refused to liquefy at the temperature of —166° (—74°·4C) while subjected to pressures varying in the different cases from 27 to 58 atmospheres.[2]

Sir Isambard Brunel, and, more recently, M. Thilorier, of Paris, succeeded in obtaining liquid carbonic acid in great abundance. The apparatus of M. Thilorier (fig. 41) consists of a pair of extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast-iron or gun-metal, or, still better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of a peculiar kind, the workmanship of which must be excellent. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution taken to prevent leakage under the enormous pressure the vessel has to bear. The receiver resembles the retort in every respect; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

The operation is thus conducted: $2\frac{3}{4}$ lb. of bicarbonate of soda, and $6\frac{1}{2}$ lb. of water at 100° (37°·7C), are introduced into the generator; oil of vitriol

[1] Phil. Trans. for 1823, p. 189.
[2] Phil. Trans. for 1845, p. 155.

Fig. 41.



to the amount of 1½ lb. is poured into a copper cylindrical vessel, whic lowered down into the mixture, and set upright; the stop-cock is screwed into its place, and forced home by a spanner and mallet. The chine is next tilted up on its trunnions, that the acid may run out of cylinder and mix with the other contents of the generator; and this mix is favoured by swinging the whole backwards and forwards for a few nutes, after which it may be suffered to remain a little time at rest.

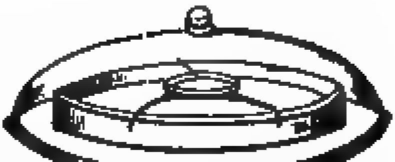
The receiver, surrounded with ice, is next connected to the generator, both cocks opened; the liquefied carbonic acid distils over into the co vessel, and there again in part condenses. The cocks are now closed, vessels disconnected, the cock of the generator opened to allow the contai gas to escape; and, lastly, when the issue of gas *has quite ceased*, the s cock itself unscrewed, and the sulphate of soda turned out. This opera must be repeated five or six times before any very considerable quantity liquefied acid will have accumulated in the receiver. When the rece thus charged has its stop-cock opened, a stream of the liquid is forc driven up the tube by the elasticity of the gas contained in the upper of the vessel.

It will be quite proper to point out to the experimenter the great pers danger he incurs in using this apparatus, unless the greatest care be ta in its management. A dreadful accident has already occurred in Paris the bursting of one of the iron vessels.

The cold produced by evaporation has been already adverted to; i simply an effect arising from the conversion of sensible heat into latent the rising vapour, and it may be illustrated in a variety of ways. A l ether dropped on the hand thus produces the sensation of great cold, water contained in a thin glass tube, surrounded by a bit of rag, is spee *frozen when the rag is* kept wetted with ether.

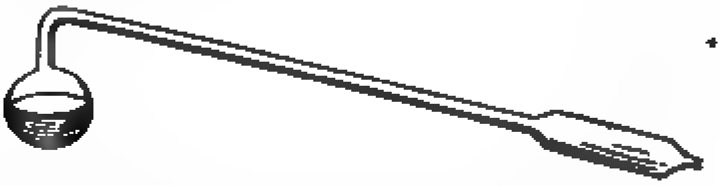
When a little water is put into a watch-glass, (fig. 42), supported by a triangle of wire over a shallow glass dish of sulphuric acid placed on the plate of a good air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a solid mass of ice, and the watch-glass very frequently broken by the expansion of the lower portion of water in the act of freezing, a thick crust first forming on the surface. The absence of the impediment of the air, and the rapid absorption of watery vapour by the oil of vitriol, induce such quick evaporation that the water has its temperature almost immediately reduced to the freezing-point.

Fig. 42.



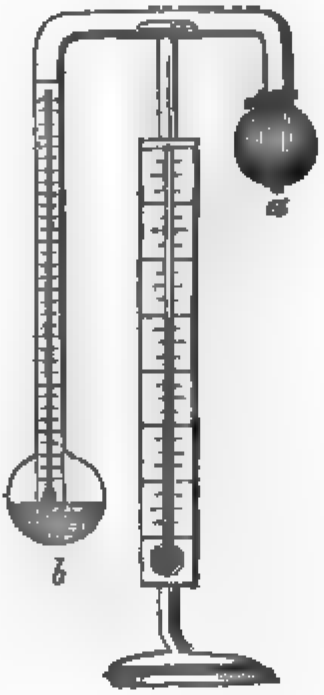
The same fact is shown by a beautiful instrument contrived by Dr. Wollaston, called a *cryophorus*, or frost-carrier. It is made of glass, of the form represented in fig. 43, and contains a small quantity of water, the rest of the space being vacuous. When all the water is turned into the bulb, and the empty extremity plunged into a mixture of ice and salt, the solidification of the vapour gives rise to such a quick evaporation from the surface of the water, that the latter freezes.

Fig. 43.



All means of producing artificial cold yield to that derived from the evaporation of the liquefied carbonic acid, just mentioned. When a jet of that liquid is allowed to issue into the air from a narrow aperture, such an intense degree of cold is produced by the vaporization of a part, that the remainder freezes to a solid, and falls in a shower of snow. By suffering this jet of liquid to flow into a metal box provided for the purpose, shown in the drawing of the apparatus (fig. 44), a large quantity of the solid acid may be obtained; it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. Mixed with a little ether, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained. The addition of the ether facilitates the contact of the carbonic acid with the mercury.

Fig. 44.



The temperature of a mixture of solid carbonic acid and ether in the air, measured by a spirit-thermometer, was found to be —106° (—76°·6C); when the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sank to —166° (—110°C). This was the method of obtaining extreme cold employed by *Mr. Faraday* in his last experiments *on the liquefaction of* gases. Under such circum-

stances, the liquefied hydriodic, hydrobromic, and sulphurous acid gases, carbonic acid, nitrous oxide, sulphuretted hydrogen, cyanogen, and ammonia, froze to colourless transparent *solids*, and alcohol became thick and oily.

The principle of the cryophorus has been very happily applied by Mr. Daniell to the construction of a dew-point hygrometer: fig. 44. It consists of a bent glass tube terminated by two bulbs, one of which is half filled with ether, the whole being vacuous as respects atmospheric air. A delicate thermometer is contained in the longer limb, the bulb of which dips into the ether; a second thermometer on the stand serves to show the actual temperature of the air. The upper bulb is covered with a bit of muslin. When an observation is to be made, the liquid is all transferred to the lower bulb, and ether dropped upon the upper one, until by the cooling effects of evaporation a distillation of the contained liquid takes place from one part of the apparatus to the other, by which such a reduction of temperature of the ether is brought about, that dew is deposited on the outside of the bulb, which is made of black glass in order that it may be more easily seen. The difference of temperature indicated by the two thermometers is then read off.

CAPACITY FOR HEAT; SPECIFIC HEAT.

Let the reader renew a supposition made when the doctrine of latent heat was under consideration; let him imagine the existence of an uniform source of heat, and its intensity such as to raise a given weight of water 10° (5°·5C) in 30 minutes. If, now, the experiment be repeated with equal weights of mercury and oil, it will be found, that instead of 30 minutes, 1 minute will suffice in the former case, and 15 minutes in the latter.

This experiment serves to point out the very important fact, that different bodies have different *capacities for heat;* that equal weights of water, oil, and mercury, require, in order to rise through the same range of temperature, quantities of heat in proportion of the numbers 30, 15, and 1. This is often expressed by saying that the *specific heat* of water is 30 times as great as that of mercury, and the specific heat of oil 15 times as great.

Again, if equal weights of water at 100° (37°·7C), and oil at 40° (4°·4C), be agitated together, the temperature of the whole will be found to be 80° (26°·6C), instead of 70° (21°·1C), the mean of the two; and if the temperatures be reversed, that of the mixture will be only 60° (15°·5C). Thus,

1 lb. water at 100° (37°·7C)
1 lb. oil at 40° (4°·4C) } give a mixture at 80° (26°·6C); hence

Loss by the water, 20° (11°·1C).
Gain by the oil, 40° (22°·2C).

1 lb. water at 40° (4°·4C)
1 lb. oil at 100° (37°·7C) } give a mixture at 60° (15°·5C); hence

Gain of water, 20° (11°·1C).
Loss of oil, 40° (22°·2C).

This shows the same fact, that water requires twice as much heat as oil to produce the same thermometric effect.

There are three distinct methods by which the specific heat of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular temperature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third is the method of mixture, on the principle illustrated; this latter method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these MM. Dulong and Petit, and recently M. Regnault, deserve especial mention. It appears that each solid and liquid has its own specific heat; and it is probable that this, in-

stead of being a constant quantity, varies with the temperature. The determination of the specific heat of gases is attended with peculiar difficulties on account of the comparatively large volume of small weights of gases. Satisfactory results have however been obtained by the method of mixing for the following gases.

SPECIFIC HEAT AT 30 INCHES PRESSURE.

	Of equal volumes.	Of equal weights. Air = 1	Water = 1
Atmospheric air	1	1	0·2669
Oxygen	1	0·8848	0·2361
Hydrogen	1	12·3401	3·2936
Nitrogen	1	1·0318	0·2754
Carbonic oxide	1	1·0805	0·2884
Protoxide of nitrogen	1·227	0·8878	0·2369
Carbonic acid	1·249	0·8280	0·2210
Olefiant gas	1·754	1·5763	0·4207
Aqueous vapour	1·960	3·1360	0·8470[1]

For the comparison of the specific heat of atmospheric air with that of water, we are indebted to Count Rumford; for the comparison of the specific heat of the various gases, to Delaroche and Berard.

Whenever a gas expands, heat becomes thereby latent. Hence the amount of heat required to raise a gas to a certain temperature increases the more we allow it to expand. Dulong has found that if the amount of heat required to raise the temperature of a volume of gas (observed at the melting point of ice, and at the pressure of 30 inches) to a given height without its volume undergoing any change, be represented by 1, then if the gas is allowed to expand until the pressure is reduced again to 30 inches whilst the high temperature is kept up, the additional amount of heat which is required for this purpose is, for oxygen, hydrogen, or nitrogen 0,421; for carbonic acid 0,423; for binoxide of nitrogen 0,343; and for olefiant gas 0,240.

If there be no source of heat from which this additional quantity can be obtained, then the gas is cooled during expansion, a portion of the free heat becoming latent. On the other hand, if a gas be compressed, this latent heat becomes free, and causes an elevation of temperature, which, under favourable circumstances, may be raised to ignition; syringes by which tinder is kindled are constructed on this principle. In the upper regions of the atmosphere the cold is intense; snow covers the highest mountain-tops even within the tropics, and this is due to the increased capacity for heat of the expanded air.

MM. Dulong and Petit observed in the course of their investigation a most remarkable circumstance. If the specific heats of bodies be computed upon equal weights, numbers are obtained, all different, and exhibiting no simple relations among themselves; but if, instead of equal weights, quantities be taken in the proportion of the chemical equivalents, an almost perfect coincidence in the numbers will be observed, showing that some exceedingly intimate connexion must exist between the relations of bodies to heat and their chemical nature; and when the circumstance is taken into view, that relations of even a still closer kind link together chemical and electrical phenomena, it is not too much to expect that ere long some law may be discovered far more general than any with which we are yet acquainted.

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[1] The later determinations of Regnault vary from the above: thus in equal weights, Water = 1; Atmospheric air he gives as 0·2377; Oxygen, 0·2182; Nitrogen, 0·2440; and Vapour of Water, 0·4750; and contrary to the results of Gay-Lussac, the specific heat of air does not vary with the temperature.—R. B.

The following table is extracted from the memoirs of M. Regnault, with whose results most of the experiments of Dulong and Petit closely coincide.

Substances.	Specific heat of equal weights.	Specific heat of equivalent weights.
Water	1·00000	
Oil of Turpentine	0·42593	
Glass	0·19768	
Iron	0·11379	3·0928
Zinc	0·09555	3·0872
Copper	0·09515	3·0172
Lead	0·03140	3·2581
Tin	0·05628	3·3121
Nickel	0·10863	3·2176
Cobalt	0·10696	3·1628
Platinum	0·03243	3·2054
Sulphur	0·20259	3·2657
Mercury	0·03332	3·7128
Silver	0·05701	6·1742
Arsenic	0·08140	6·1326
Antimony	0·05077	6·5615
Gold	0·03244	6·4623
Iodine	0·05412	6·8462
Bismuth	0·03084	2·1877

Of the numbers in the second column, the first ten approximate far too closely to each other to be the result of mere accidental coincidence; the five that follow are very nearly twice as great; and the last is one-third less.[1]

Independently of experimental errors, there are many circumstances which tend to show, that, if all modifying causes could be compensated, or their effects allowed for, the law might be rigorously true.

The observations thus made upon elementary substances have been extended by M. Regnault to a long series of compounds, and the same curious law found, with the above limitations, to prevail throughout, save in a few isolated cases, of which an explanation can perhaps be given.

Except in the case of certain metallic alloys, where the specific heats were the mean of those of their constituent metals, no obvious relation can be traced between the specific heat of the compound body and of its components. The most general expression of the facts that can be given is the following:—

In bodies of similar chemical constitution, the specific heats are in an inverse ratio to the equivalent weights, or to a multiple or submultiple of the latter.— Simple as well as compound bodies will be comprehended in this law.[2]

SOURCES OF HEAT.

The first and greatest source of heat, compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by rays of a heating nature, which, striking against the surface of the earth, elevate its temperature; this heat is communicated to the air by convection, as already described, air and gases in general not being sensibly heated by the passage of the rays.

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[1] The equivalent of Bismuth being assumed as 71, but adopting 213, the number given under the head of bismuth, the specific heat of an equivalent weight will be 6·5688, or coincide with the five preceding.—R. B.

[2] Ann. Chim. et Phys. lxxiii [illegible] same, 3rd series, i. 129.

A second source of heat is supposed to exist in the interior of the earth. It has been observed, that in sinking mine-shafts, boring for water, &c., the temperature rises in descending, at the rate, it is said, of about 1° ($\frac{5}{9}$°C) for every 45 feet, or 117° (65°C) per mile. On the supposition that the rise continued at the same rate, at the depth of less than two miles the earth would have the temperature of boiling water; at nine miles it would be red hot; and at 30 or 40 miles depth, all known substances would be in a state of fusion.[1]

According to this idea, the earth must be looked upon as an intensely-heated, fluid spheroid, covered with a crust of solid badly-conducting matter, cooled by radiation into space, and bearing somewhat the same proportion in thickness to the ignited liquid within, that the shell of an egg does to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact; that the figure of the earth is really such as would be assumed by a fluid mass; and, lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

The smaller, and what may be called secondary, sources of heat, are very numerous; they may be divided, for the present, into two groups, mechanical motion and chemical combination. To the first must be referred elevation of temperature by friction and blows; and to the second, the effects of combustion and animal respiration. With regard to the heat developed by friction, it appears to be indefinite in amount, and principally dependent upon the nature of the rubbing surfaces. An experiment of Count Rumford is on record, in which the heat developed by the boring of a brass cannon was sufficient to bring to the boiling-point two and a half gallons of water, while the dust or shavings of metal, cut by the borer, weighed a few ounces only. Sir H. Davy melted two pieces of ice by rubbing them together in vacuo at 32° (0°C); and uncivilized men, in various parts of the world, have long been known to obtain fire by rubbing together two pieces of dry wood. The origin of the heat in these cases is by no means intelligible.

Malleable metals, as iron and copper, which become heated by hammering or powerful pressure, are found thereby to have their density sensibly increased and their capacity for heat diminished; the rise of temperature is thus in some measure explained. A soft iron nail may be made red-hot by a few dexterous blows on an anvil; but the experiment cannot be repeated until the metal has been *annealed*, and in that manner restored to its original physical state.

The disengagement of heat in the act of combination is a phenomenon of the utmost generality. The quantity of heat given out in each particular case is in all probability fixed and definite; its intensity is dependent upon the time over which the action is extended. Science has already been enriched by many admirable, although yet incomplete, researches on this important but most difficult subject.

It is not improbable that many of the phenomena of heat, classed at present under different heads, may hereafter be referred to one common cause, namely, alterations in the capacity for heat of the same body under different

[1] The new Artesian well at Grenelle, near Paris, has a depth of 1794·5 English feet: it is bored through the chalk basin to the sand beneath; the work occupied seven years and two months. The temperature of the water, which is exceedingly abundant, is 82° (27°·7C); the mean temperature of Paris is 51° (10°·5C); the difference is 31° (17°·2C), which gives a rate of about 1° ($\frac{5}{9}$°C) for 58 feet.

physical conditions. For example, the definite absorption and evolution of sensible heat attending change of state may be simply due to the increased capacity for heat, to a fixed and definite amount, of the liquid over the solid, and the vapour over the liquid. The experimental proof of the facts is yet generally wanting; in the very important case of water, however, the decidedly inferior capacity for heat of ice compared with that of liquid water seems fully proved from experiments on record.

The heat of combination might perhaps, in like manner, be traced to condensation of volume, and the diminution of capacity for heat which almost invariably attends condensation. The proof of the proposition in numerous cases would be within the reach of comparatively easy experimental inquiry.

LIGHT.

The subject of light is so little connected with elementary chemistry, that a very slight notice of some of the most important points will suffice.

Two views have been entertained respecting the nature of light. Sir Isaac Newton imagined that luminous bodies emitted, or shot out, infinitely small particles in straight lines, which, by penetrating the transparent part of the eye and falling upon the nervous tissue, produced vision. Other philosophers drew a parallel between the properties of light and those of sound, and considered, that as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances, to which they gave the name of *ether*. The wave-hypothesis of light is at present most in favour, as it serves to explain certain singular phenomena, discovered since the time of Newton, with greater facility than the other.

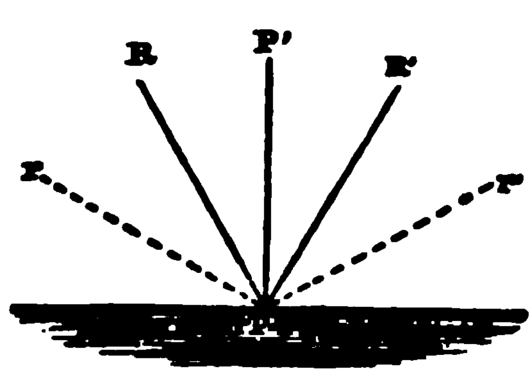
A ray of light emitted from a luminous body proceeds in a straight line, and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time required by each satellite for the purpose, is exactly known from its periodical entry into or exit from the shadow of the planet. The time required by one is only 42 hours. Römer, the astronomer, at Copenhagen, found that this period appeared to be longer when the earth, in its passage round the sun, was most distant from the planet Jupiter, and, on the contrary, he observed that the periodic time appeared to be shorter when the earth was nearest to Jupiter. The difference, though very small, for a single revolution of the satellite, by the addition of many, so increases, during the passage of the earth from its nearest to its greatest distance from Jupiter, that is, in about half a year, that it amounts to 16 minutes and 16 seconds. Römer concluded from this, that the light of the sun reflected from the satellite, required that time to pass through a distance equal to the diameter of the orbit of the earth, and since this space is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen hereafter that this rapidity of transmission is rivalled by that of the electrical agent.

When a ray of light falls on a plane surface it may be disposed of in three ways; it may be absorbed and disappear altogether; it may be reflected, or thrown off, according to a particular law; or it may be partly absorbed, partly reflected, and partly transmitted. The first happens when the surface is perfectly black and destitute of lustre; the second, when a polished surface of any kind is employed; and the third, when the body upon which the light falls is of the kind called transparent, as glass or water.

The law of reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular measured, it will be found that the ray, after reflection, takes such a course as to make with the perpendicular

an equal angle on the opposite of the latter. A ray of light, R, fig. falling at the point P, will be reflected the direction PR′, making the angle R′ equal to the angle RPP′; or a ray fr the point r falling upon the same spot be reflected to r′ in virtue of the sa law. Farther, it is to be observed, t the incident and reflected rays are alw contained in the same vertical plane.

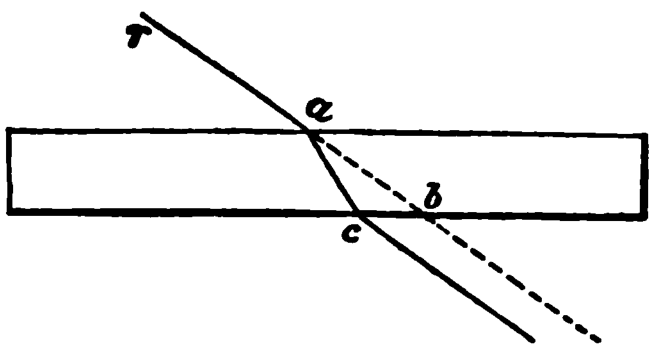
Fig. 45.



The same rule holds good if the mir be curved, as a portion of a sphere, curve being considered as made up c multitude of little planes. Parallel r become permanently altered in direction when reflected from curved surfa becoming divergent or convergent according to the kind of curvature.

It has just been stated that light passes in straight lines; but this is c true so long as the medium through which it travels preserves the sa density and the same chemical nature; when this ceases to be the case, ray of light is bent from its cou into a new one, or, in optical l guage, is said to be *refracted.*

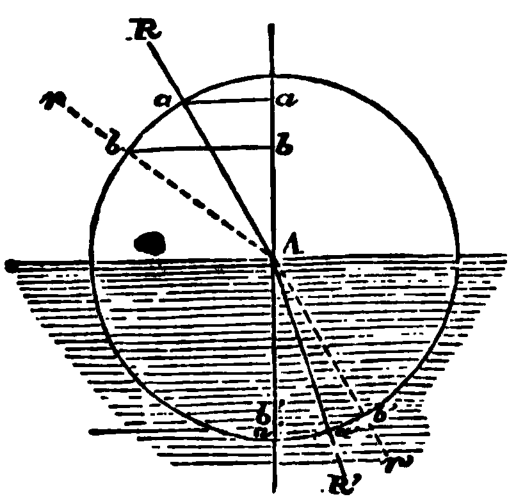
Fig. 46.



Let *r*, fig. 46, be a ray of li falling upon a plate of some tra parent substance with parallel si such as a piece of thick plate gla and *a* its point of contact with upper surface. The ray, inst of holding a straight course passing into the glass in the dir tion *a b*, will be bent downwa to *c*; and, on leaving the glass, and issuing into the air on the other s it will again be bent, but in the opposite direction, so as to make it para to the continuation of its former track. The general law is thus express —When the ray passes from a rare to a denser medium, it is usually refrac *towards* a line perpendicular to the surface of the latter; and convers when it leaves a dense medium for a rarer one, it is refracted *from* a perpendicular to the surface of the denser substance: in the former c the angle of incidence is said to be greater than that of refraction; in latter, it is said to be less.

The amount of refraction, for the same medium, varies with the obliqu with which the ray strikes the surface. W perpendicular to the latter, it passes with change of direction at all; and in other p tions, the refraction increases with the o quity.

Fig. 47.



Let R, fig. 47, represent a ray of light f ing upon the surface of a mass of plate gl at the point A. From this point let a perp dicular be raised and continued into the n medium, and around the same point, a centre, let a circle be drawn. According the law just stated, the refraction must be wards the perpendicular; in the direction . for example. Let the lines *a*—*a*, *a′*—*a′*, right angles to the perpendicular, be draw and their length compared by means of a scale of equal parts, and not

their length will be in the case supposed in the proportion of 3 to 2. These lines are termed the sines of the angles of incidence and refraction, respectively.

Now let another ray be taken, such as *r*; it is refracted in the same manner to *r′*, the bending being greater from the increased obliquity of the ray; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared they will still be found to bear to each other the proportion of 3 to 2. The fact is expressed by saying, that the *ratio of the sines of the incidence and refraction is constant for the same medium.*

The plane of refraction coincides moreover with that of incidence.

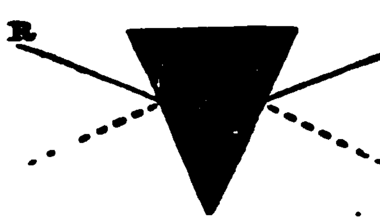
Different bodies possess different refractive powers; generally speaking, the densest substances refract most. Combustible bodies have been noticed to possess greater refractive power than their density would indicate, and from this observation Sir I. Newton predicted the combustible nature of the diamond long before anything was known respecting its chemical nature.

The method adopted for describing the comparative refractive powers of different bodies is to state the ratio borne by the sine of the angle of refraction to that of incidence, making the former unity: this is called the *index of refraction* for the substance. Thus, in the case of glass, the index of refraction will be 1·5. When this is once known for any particular transparent body, the effect of the latter upon a ray of light entering it, in any position, can be calculated by the aid of the law of sines.

Substances.	Index of refraction.	Substances.	Index of refraction.
Tabasheer[1]	1·10	Garnet	1·80
Ice	1·30	Glass, with much oxide of lead	1·90
Water	1·34	Zircon	2·00
Fluor spar	1·40	Phosphorus	2·20
Plate glass	1·50	Diamond	2·50
Rock crystal	1·60	Chromate of lead	3·00
Crysolite	1·69		
Bisulphide of carbon	1·70		

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example.—Let fig. 48 represent a triangular prism of glass, upon the side of which the ray of light R may be supposed to fall. This ray will of course be refracted in entering the glass towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface on emerging into the air. The result will be a total change in the direction of the ray.

Fig. 48.

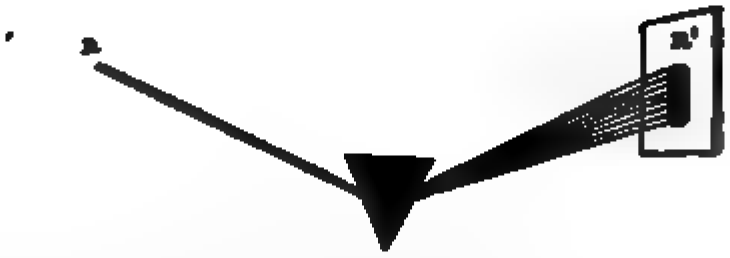


A convex lens is thus enabled to converge rays of light falling upon it, and a concave lens to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

The light of the sun and celestial bodies in general, as well as that of the electric spark, and of all ordinary flames, is of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in the shutter, or otherwise (fig. 49), and suffered to fall upon a

[1] A siliceous deposit in the joints of the bamboo.

Fig. 49.

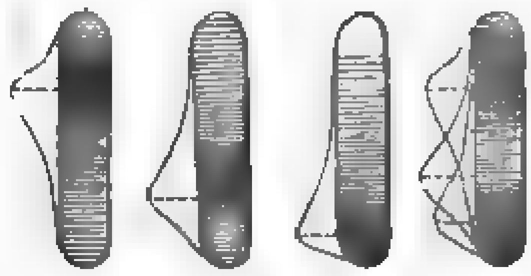


glass prism in the manner described above, it will not only be refracted from its straight course, but will be decomposed into a number of coloured rays; which may be received upon a white screen placed behind the prism. When solar light is employed, the colours are extremely brilliant, and spread into an oblong space of considerable length. The upper part of this image or *spectrum* will be violet, and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir I. Newton, and from it he drew the inference that white light is composed of seven primitive colours, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.

Sir D. Brewster is disposed to think, that out of Newton's seven primitive colours four are really compound, and formed by the superposition of the three remaining, namely, blue, yellow, and red, which alone deserve the name of primitive. When these three kinds of rays are mixed, or superimposed, in a certain definite manner, they produce white light, but when one or two of them are in excess, then an effect of colour is perceptible, simple in the first case, and compound in the second. There are, according to this hypothesis, rays of all refrangibilities of each colour, and consequently white light in every part of the spectrum, but then they are unequally distributed; the blue rays are more numerous near the top, the yellow towards the middle, and the red at the bottom, the excess of each colour producing its characteristic effect. In the diagram below (fig. 50) the intensity of each colour is represented by the height of a curve, and the effects of mixture will be intelligible by a little consideration.

Fig. 50.

BLUE. YELLOW. RED. SOLAR SPECTRUM.



VIOLET.
INDIGO.
BLUE.
GREEN.
YELLOW.
ORANGE.
RED.

Bodies of the same mean refractive power do not always equally disperse or spread out the differently coloured rays; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet shall be similarly affected. Hence, prisms of different varieties of glass, or other transparent *substances*, give, under similar circumstances, very different spectra, both

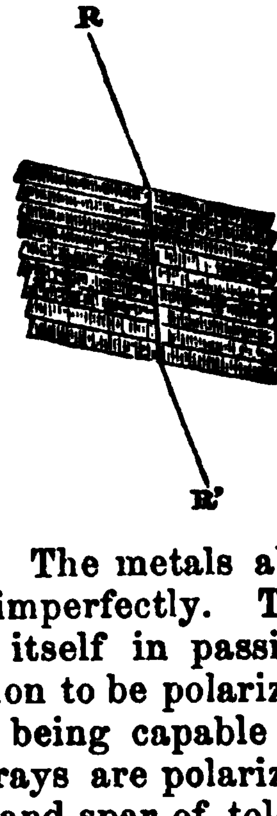
as respects the length of the image, and the relative extent of the coloured bands.

The colours of natural objects are supposed to result from the power which the surfaces of the bodies possess of absorbing some of the coloured rays, while they reflect or transmit, as the case may be, the remainder. Thus, an object appears red because it absorbs, or causes to disappear, a portion of the yellow and blue rays composing the white light by which it is illuminated.

A ray of common light made to pass through certain crystals of a particular order is found to undergo a very remarkable change. It becomes split or divided into two rays, one of which follows the general law of refraction, and the other takes a new and extraordinary course, dependent on the position of the crystal. This effect, which is called double refraction, is beautifully illustrated in the case of Iceland spar, or crystallized carbonate of lime. On placing a rhomb of this substance on a piece of white paper, on which a mark or line has been made, the object will be seen double.

Again, if a ray of light be suffered to fall upon a plate of glass at an angle of 56° 45′, the portion of the ray which suffers reflection will be found to have acquired properties which it did not before possess; for on throwing it, under the same angle, upon a second glass plate, it will be observed that there are two particular positions of the latter in which the ray ceases to be reflected. Light which has suffered this change is said to be *polarized*.

Fig. 51.



The light which passes through the first or polarizing plate, is also to a certain extent in this peculiar condition, and by employing a series of similar plates (fig. 51), held parallel to the first, this effect may be greatly increased; a bundle of fifteen or twenty such plates may be used with great convenience for the experiment. It is to be remarked, also, that the light polarized by transmission in this manner is in an opposite state to that polarized by reflection; that is, when examined by a second or *analyzing* plate, held at the angle before mentioned, it will be seen to be reflected when the other disappears, and to be absorbed when the first is reflected.

It is not every substance which is capable of polarizing light in this manner; glass, water, and certain other bodies, bring about the change in question, each having a particular polarizing angle at which the effect is greatest. The metals also can, by reflection, polarize the light, but they do so very imperfectly. The two rays into which a pencil of common light divides itself in passing through a doubly-refracting crystal are found on examination to be polarized in a very complete manner, and also transversely, the one being capable of reflection when the other vanishes. It is said that both rays are polarized in opposite directions. With a rhomb of transparent Iceland spar of tolerably large dimensions the two oppositely-polarized rays may be widely separated and examined apart.

There is yet another method of polarization, by the employment of plates of the mineral tourmaline cut parallel to the axis of the crystal. This body polarizes by simple transmission, the ray falling perpendicular to its surface; a part of the light is absorbed, and the remainder modified in the manner described. When two such plates are held with their axes parallel, as in fig. 52, light traverses them both freely; but when one of them is turned round in the manner shown in fig. 53, so as to make the axes cross at right angles, the light is almost wholly stopped, if the tourmalines be good. A plate of the mineral thus becomes an excellent test for discriminating between the polarized light and that which has not undergone the change.

Some of the most splendid phenomena of the science of light are exhibite

Fig. 52.

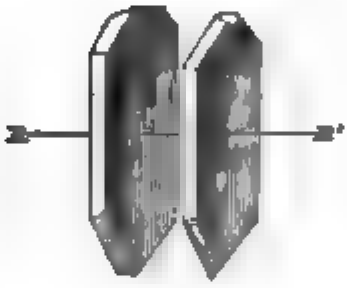
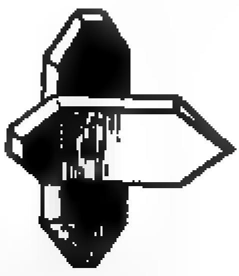


Fig. 53.



when thin plates of doubly-refracting substances are interposed between the polarizing arrangement and the analyzer.

Instead of the tourmaline plate, which is always coloured, frequent use is made of two Nichol's prisms, or conjoined prisms of carbonate of lime, which, in consequence of a peculiar cutting and combination, possess the property of allowing only one of the oppositely polarized rays to pass. If the two Nichol's prisms are placed one behind the other in precisely similar positions, the light polarized by the one goes through the other unaltered. But when one prism is slightly turned round in its setting, a cloudiness is produced, and by continuing to turn the prism this increases until perfect darkness ensues. This happens, as with the tourmaline plates, when the two prisms cross one another. The phenomenon is the same with colourless as with coloured light.

Supposing that polarized light, coloured, for example, by going through a plate of red glass, passed through the first Nichol's prism and was altogether obstructed in consequence of the position of the second prism, then if between the two prisms a plate of rock crystal, formed by a section at right angles to the principal axis of the crystal, is interposed, the light polarized by the first prism by passing through the plate of quartz is enabled partially to pass through the second Nichol's prism. Its passage through the second prism can then again be interrupted by turning the second prism round to a certain extent. The rotation required varies with the thickness of the plate of rock crystal, and also with the colour of the light that is employed. It increases from red in the following order, green, yellow, blue, violet.

This property of rock crystal was discovered by Arago. The kind of polarization has been called circular polarization. No other crystals are known to produce the same effect. The direction of the rotation is with many plates towards the right hand; in other plates it is towards the left. The one class is said to possess right-handed polarization; the other class left-handed polarization.

Biot observed that many solutions of organic substances exhibit the property of circular polarization, though to a far less extent than rock crystal. Thus, solution of cane-sugar and tartaric acid possess right-handed polarization, whilst albumen, grape-sugar, and oil of turpentine, are left-handed. In all these solutions the amount of circular polarization increases with the concentration of the fluid and the thickness of the column of liquid through which the light passes. Hence circular polarization is an important auxiliary in chemical analysis. In order to determine the amount of polarization which any fluid exhibits, the liquid is put into a glass tube not less than from ten to twelve inches long, which is closed with glass plates, one of which should be coloured, red for example. This is then placed between the two Nichol's prisms, which have previously been so arranged with regard to each other that no light could pass through. An apparatus of this description, the saccharometer, is chiefly used for determining the concentration of solutions of sugar.

ıday has made the remarkable discovery, that if a very strong electric is passed round a substance which possesses the property of circular ˙on, the amount of rotation is altered to a considerable degree.

inous rays of the sun are accompanied, as already mentioned, by ıich possess heating powers. If the temperature of the different ˍd spaces in the spectrum be tried with a delicate thermometer, it ɔe found to increase from the violet to the red extremity, and when the ɔsm is of some particular kinds of glass, the greatest effect will be maniest a little beyond the visible red ray. It is inferred from this that the chief mass of the heating rays of the sun are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, could be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light, and parallel cases occur in great numbers in organic chemistry: the blackening and decomposition of salts of silver are familiar instances of the chemical powers of the same agent. Now it is not the luminous part of the ray which effects these changes; they are produced by certain invisible rays accompanying the others, and which are found most abundantly in and beyond the violet part of the spectrum. It is there that the chemical effects are most marked, although the intensity of the light is exceedingly feeble. The chemical rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect.

In the year 1802,[1] Mr. Thomas Wedgwood proposed a method of copying paintings on glass by placing behind them white paper or leather moistened with a solution of nitrate of silver, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and only examined by candle-light, otherwise they became obliterated by the blackening of the whole surface from which the salt of silver could not be removed. These attempts at light-painting attracted but little notice till the publication of Mr. Fox Talbot's[2] papers, read before the Royal Society, in January and February, 1839, in which he detailed two methods of fixing the pictures produced by the action of light on paper impregnated with chloride of silver, and at the same time described a plan by which the sensibility of the prepared paper may be increased to the extent required for receiving impressions from the images of the camera obscura.

Very shortly afterwards, Sir John Herschel[3] proposed to employ solutions of the alkaline hyposulphites for removing the excess of chloride of silver from the paper, and thus preventing the farther action of light, and this plan has been found exceedingly successful. The greatest improvement, however, which the curious art of photogenic drawing has received, is due to Mr. Talbot,[4] who, in a communication to the Royal Society, described a method by which paper of such sensibility could be prepared as to permit its application to the taking of portraits of living persons by the aid of a good camera obscura, the time required for a perfect impression never exceeding a few minutes. The portraits executed in this manner by Mr. Collen and others are beautiful in the highest degree, and leave little room for improvement in any respect. The process itself is rather complex, and

[1] Journal of the Royal Institution, i. 170.
[2] Phil. Mag. March, 1839
[3] Phil. Trans. for 1840, p. 1.
[4] Phil. Mag. August, 1841.

demands a great number of minute precautions, only to be learned by experience, but which are indispensable to perfect success. The general plan is the following:—

Writing-paper of good quality is washed on one side with a moderately dilute solution of nitrate of silver, and left to dry spontaneously in a dark room; when dry, it is dipped into a solution of iodide of potassium, and again dried. These operations should be performed by candle-light. When required for use, the paper thus coated with yellow iodide of silver is brushed over with a solution containing nitrate of silver, acetic acid, and gallic acid, and once more carefully dried by gentle warmth. This *kalotype* paper is so sensitive, that exposure to diffused daylight for one second suffices to make an impression upon it, and even the light of the moon produces the same effect, although a much longer time is required.

The images of the camera obscura are at first invisible, but are made to appear in full intensity by once more washing the paper with the above mentioned mixture, and warming it before the fire, when the blackening effect commences and reaches its maximum in a few minutes.

The picture is of course *negative*, the lights and shadows being reversed; to obtain *positive* copies nothing more is necessary than to place a piece of ordinary photographic paper prepared with chloride of silver beneath the kalotype impression, cover them with a glass plate, and expose the whole to the light of the sun for a short time. Before this can be done, the kalotype must however be fixed, otherwise it will blacken, and this is effected by immersion in a solution of hyposulphite of soda, and well washing with water.

Sir John Herschel has shown that a great number of other substances can be employed in these photographic processes by taking advantage of the singular deoxidizing effects of certain portions of the solar rays. Paper washed with a solution of a salt of sesquioxide of iron becomes capable of receiving impressions of this kind, which may afterwards be made evident by ferricyanide of potassium, or terchloride of gold. Vegetable colours are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.[1]

The Daguerreotype, the announcement of which was first made in the summer of 1839 by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly-polished plate of silvered copper is exposed for a certain period to the vapour of iodine, and then transported to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of iodide of silver. The picture, however, only becomes visible by exposing it to the vapour of mercury, which attaches itself, in the form of exceedingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the drawing is washed with a solution of hyposulphite of soda to remove the undecomposed iodide of silver, and render it permanent.

The images of objects thus produced bear the most minute examination with a magnifying glass, the smallest details being depicted with perfect fidelity.

Great improvements have been necessarily made in the application of this beautiful art to taking portraits. By the joint use of bromine and iodine the plates are rendered far more sensitive, and the time of sitting is shortened to a very few seconds. When the operation is completed the colour of the plate is much improved by the deposition of an exceedingly thin film of gold, which communicates a warm purplish tint, and removes the previous dull leaden-grey hue, to most persons very offensive.

[1] Phil. Trans. 1842, p. 1.

RADIATION, REFLECTION, ABSORPTION, AND TRANSMISSION OF HEAT.

RADIATION OF HEAT.

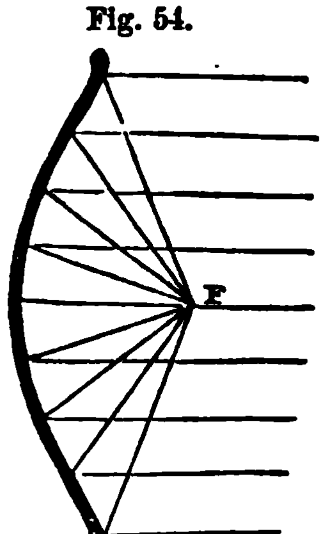
If a red-hot ball be placed upon a metallic support, and left to itself, cooling immediately commences, and only stops when the temperature of the ball is reduced to that of the surrounding air. This effect takes place in three ways: heat is conducted away from the ball through the substance of the support; another portion is removed by the convective power of the air; and the residue is thrown off from the heated body in straight lines or rays, which pass through air without interruption, and become absorbed by the surfaces of neighbouring objects which happen to be presented to their impact.

This radiant or radiated heat resembles, in very many respects, ordinary light; it suffers reflection from polished surfaces according to the same law; it is absorbed by those that are dull or rough; it moves with extreme velocity; and, finally, it traverses certain transparent media, undergoing refraction at the same time, in obedience to the laws which regulate that phenomenon in optics.

The fact of the *reflection* of heat may be very easily proved. If a person stand before a fire in such a position that his face may be screened by the mantelshelf, and if he then take a bright piece of metal, as a sheet of tinned plate, and hold it in such a manner that the fire may be seen by reflection, at the same moment a distinct sensation of heat will be felt.

The apparatus best fitted for studying these facts consists of a pair of concave metallic mirrors of the form called parabolic. The parabola is a curve possessing very peculiar properties, one of the most prominent being the following: — A tangent drawn to any part of the curve makes equal angles with two lines, one of which proceeds from the point where the tangent touches the curve in a direction parallel to what is called the axis of the parabola, and the other from the same spot through a point in front of the curve, called the focus. It results from this that parallel rays, either of light or heat, falling upon a mirror of this particular curvature in a direction parallel to the axis of the parabola, will be all reflected to a single point at the focus; and rays diverging from this focus, and impinging upon the mirror, will, after reflection, become parallel (fig. 54).

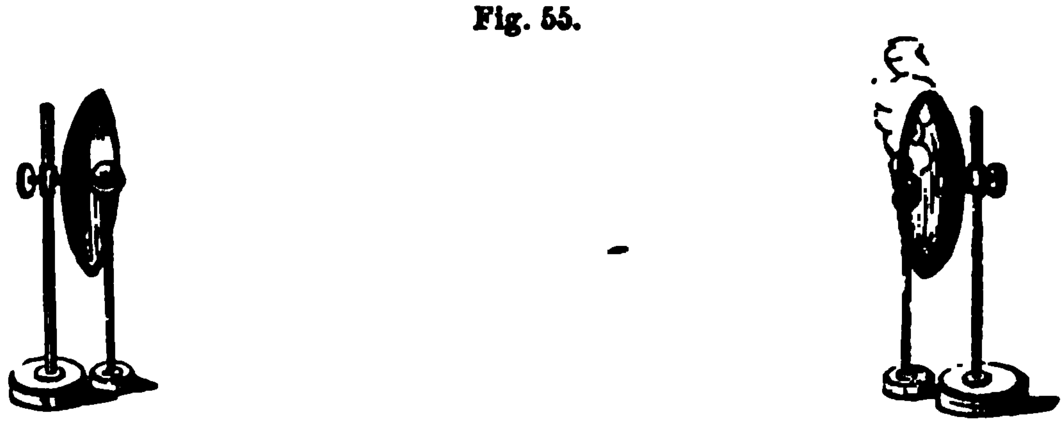
Fig. 54.



If two such mirrors be placed opposite to each other at a considerable distance, and so adjusted that their axes shall be coincident, and a hot body placed in the focus of the one, while a thermometer occupies that of the other, the reflection of the rays of heat will become manifest by their effect upon the instrument. In this manner, with a pair of by no means very perfect mirrors, 18 inches in diameter, separated by an interval of 20 feet or more, amadou or

gunpowder may be readily fired by a red-hot ball in the focus of the opposite mirror (fig. 55).

Fig. 55.



The power of radiation varies exceedingly with different bodies, as may be easily proved. If two similar vessels of equal capacity be constructed of thin metal, and the surface of one highly polished, while that of the other is covered with lampblack, and both filled with hot water of the same temperature, and their rate of cooling observed from time to time with a thermometer, it will be constantly found that the blackened vessel loses heat much faster than the one with bright surfaces; and since both are put on a footing of equality in other respects, this difference, which will often amount to many degrees, must be ascribed to the superior emissive power of the film of soot.

By another arrangement, a numerical comparison can be made of these differences. A cubical metallic vessel is prepared, each of whose sides is in a different condition, one being polished, another rough, a third covered with lampblack, &c. This vessel is filled with water, kept constantly at 212° (100°C) by a small steam-pipe. Each of its sides is then presented in succession to a good parabolic mirror, having in its focus one of the bulbs of the differential thermometer before described (fig. 22), the bulb itself being blackened. The effect produced on this instrument is taken as a measure of the comparative radiating powers of the different surfaces. The late Sir John Leslie obtained by this method of experiment the following results: —

	Emissive power.		Emissive power.
Lampblack	100	Tarnished lead	45
Writing-paper	98	Clean lead	19
Glass	90	Polished iron	15
Plumbago	75	Polished silver	12

The best reflecting surfaces are always the worst radiators; polished metal reflects nearly all the heat that falls upon it, while its radiating power is the feeblest of any substance tried, and lampblack, which reflects nothing, radiates most perfectly.

The power of *absorbing* heat is in direct proportion to the power of emission. The polished metal mirror, in the experiment with the red-hot ball, remains quite cold, although only a few inches from the latter; or, again, if a piece of gold leaf be laid upon paper, and a heated iron held over it

[1] The formerly supposed influence of mere difference of surface has been called in question by M. Melloni, who attributes to other causes the effects observed by Sir John Leslie and others, among which superficial oxidation and difference of physical condition with respect to hardness and density, are among the most important. With metals not subject to tarnish, scratching the surface *increases* the emissive power when the plates have been rolled or hammered, *i. e.* are in a compressed state, and diminishes it, on the contrary, when the metal has been cast and carefully polished without burnishing. In the case of ivory, marble, and jet, where compression cannot take place, no difference is perceptible in the radiating power of polished and rough surfaces. — Ann. Chim. et Phys. lxx. 435.

until the paper is completely scorched, it will be found that the film of metal has perfectly defended that portion beneath it.

The faculty of absorption seems to be a good deal influenced by colour; Dr. Franklin found that when pieces of cloth of various colours were placed on snow exposed to the feeble sunshine of winter, the snow beneath them became unequally melted, the effect being always in proportion to the depth of the colour; and Dr. Stark has since obtained a similar result by a different method of experimenting. According to the late researches of Melloni, this effect depends less on the colour than on the nature of the colouring matter which covers the surface of the cloth.

These facts afford an explanation of two very interesting and important natural phenomena, namely, the origin of dew, and the cause of the land and sea-breezes of tropical countries. While the sun remains above the horizon, the heat radiated by the surface of the earth into space is compensated by the absorption of the solar beams; but when the sun sets, and this supply ceases, while the emission of heat goes on as actively as before, the surface becomes cooled until its temperature sinks below that of the air. The air in contact with the earth of course participates in this reduction of temperature; the aqueous vapour present speedily reaches its point of maximum density, and then begins to deposit moisture, whose quantity will depend upon the proportion of vapour in the atmosphere, and on the extent to which the cooling process has been carried.

It is observed that dew is most abundant in a clear calm night, succeeding a hot day; under these circumstances the quantity of vapour in the air is usually very great, and at the same time, radiation proceeds with most facility. At such times a thermometer laid on the ground will, after some time, indicate a temperature of 10° (5°·5C), 15° (8°·3C), or even 20° (11°·1C) below that of the air a few feet higher. Clouds hinder the formation of dew, by reflecting back to the earth the heat radiated from its surface, and thus preventing the necessary reduction of temperature; and the same effect is produced by a screen of the thinnest material stretched at a little height above the ground. In this manner gardeners often preserve delicate plants from destruction by the frosts of spring and autumn. The piercing cold felt just before and at sunrise, even in the height of summer, is the consequence of this refrigeration having reached its maximum.

Wind also effectually prevents the deposition of dew, by constantly renewing the air lying upon the earth before it has had its temperature sufficiently reduced to cause condensation of moisture.

Many curious experiments may be made by exposing on the ground at night, bodies which differ in their powers of radiation. If a piece of black cloth and a plate of bright metal be thus treated, the former will often be found in the morning covered with dew, while the latter remains dry.

Land and sea-breezes are certain periodical winds common to most sea-coasts within the tropics, but by no means confined to those regions. It is observed, that a few hours after sunrise a breeze springs up at sea, and blows directly on shore, and that its intensity increases as the day advances, and declines and gradually expires near sunset. Shortly after, a wind arises in exactly the opposite direction, namely, from the land towards the sea, lasts the whole of the night, and only ceases with the reappearance of the sun.

It is easy to give an explanation of these effects. When the sun shines at once upon the surface of the earth and that of the sea, the two become unequally heated from their different absorbing power; the land becomes much the warmer. The air over the heated surface of the ground, being expanded by heat, rises, and has its place supplied by colder air flowing from the sea, producing the sea-breeze. When the sun sets, both sea and land begin to cool by radiation; the rate of the cooling of the latter will, how-

ever, far exceed that of the former, and its temperature will rapidly fall. The air above becoming cooled and condensed, flows outwards in obedience to the laws of fluid pressure, and displaces the warmer air of the ocean. In this manner, by an interchange of air between sea and land, the otherwise oppressive heat is moderated, to the great advantage of those who inhabit such localities. The land and sea-breezes extend to a small distance only from shore, but afford, notwithstanding, essential aid to coasting navigation, since vessels on either tack enjoy a fair wind during the greater part of both day and night.

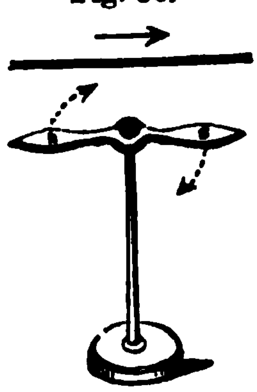
TRANSMISSION OF HEAT; DIATHERMANCY.

Rays of heat, in passing through air, receive no more obstruction than those of light under similar circumstances; but with other transparent media the case is different. If a parabolic mirror be taken and its axis directed towards the sun, the rays both of heat and light will be reflected to the focus, which will exhibit a temperature sufficiently high to fuse a piece of metal, or fire a combustible body. If a plate of glass be now placed between the mirror and the sun, the effect will be but little diminished.

Now, let the same experiment be made with the heat of a kettle filled with boiling water; the heat will be concentrated by reflection as before, but, on interposing the glass, the heating effect at the focus will be reduced to nothing. Thus, the rays of heat coming from the sun traverse glass with facility, which is not the case with those emanating from the boiling water.

In the year 1833, M. Melloni published the first of a series of exceedingly valuable researches on this subject, which are to be found in detail in various volumes of the Annales de Chemie et de Physique.[1] It will be necessary, in the first instance, to describe the method of operation followed by this philosopher.

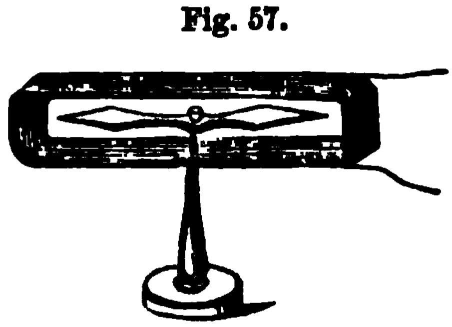
Fig. 56.



Not long before, two very remarkable facts had been discovered: Oersted, in Copenhagen, showed that a current of electricity, however produced, exercises a singular and perfectly definite action on a magnetic needle; and Seebeck, in Berlin, found that an electric current may be generated by the unequal effects of heat on different metals in contact. If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position and assume a new one, as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle (fig. 56), while the current it carries travels from north to south, the needle is deflected from its ordinary direction and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above produces the same effect as reversing the current.

When the needle is subjected to the action of two currents in opposite directions, the one above and the other below, they will obviously concur in their effects. The same thing happens when the wire carrying the current is bent upon itself (fig. 57), and the needle placed between the two portions; and since every time the bending is repeated, a fresh portion of the current is made to act in the same manner upon the needle, it is easy to see how a current too feeble to produce any effect when a simple straight wire is

Fig. 57.

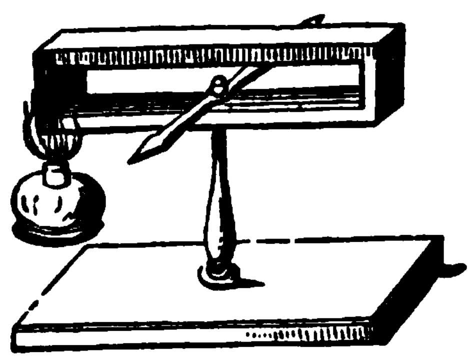


[1] Translated also in Taylor's Scientific Memoirs.

ıployed, may be made by this contrivance to exhibit a powerful action on ɜ magnet. It is on this principle that instruments called *galvanometers*, *'vanoscopes*, or *multipliers*, are constructed; they serve, not only to indicate ɜ existence of electrical currents, but to show by the effect upon the needle ɜ direction in which they are moving. By using a very long coil of wire, d two needles, immovably connected, and hung by a fine filament of silk, nost any degree of sensibility may be communicated to the apparatus.

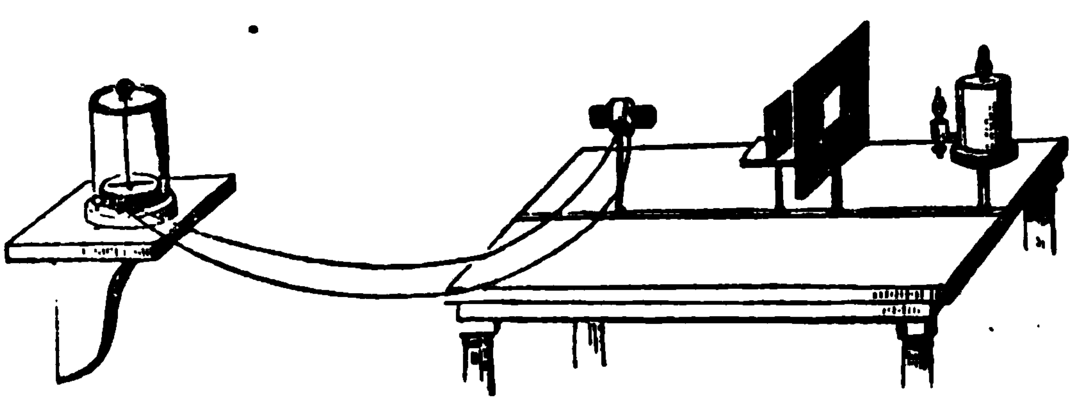
When two pieces of different metals, connected together at each end, have e of their joints more heated than the other, an electric current is imme-ιtely set up. Of all the metals tried, bismuth and antimony form the ›st powerful combination. A single pair of bars, having one of their junc-ns heated in the manner shown in fig. 58, can velop a current strong enough to deflect a npass-needle placed within, and, by ar-ıging a number in a series and heating their ernate ends, the intensity of the current may very much increased. Such an arrangement called a thermo-electric pile. M. Melloni nstructed a thermo-electric pile of this kind, ntaining fifty-five slender bars of bismuth d antimony, laid side by side and soldered ;ether at their alternate ends. He connected s pile with an exceedingly delicate multiplier, d found himself in the possession of an in-'ument for measuring small variations of temperature far surpassing in licacy the air-thermometer in its most sensitive form, and having great vantages in other respects over that instrument when employed for the rposes to which he devoted it.

Fig. 58.



The substances whose powers of transmission were to be examined were t into plates of a determinate thickness, and, after being well polished, :anged in succession in front of the little pile, the extremity of which was ıckened to promote the absorption of the rays. (Fig. 59.) A perforated

Fig. 59.



'een, the area of whose aperture equalled that of the face of the pile, s placed between the source of heat and the body under trial, while a :ond screen served to intercept all radiation until the moment of the ex-:iment.

After much preliminary labour for the purpose of testing the capabilities the apparatus and the value of its indications, an extended series of re-.rches was undertaken and carried on during a long period with great ɔcess: some of the most curious results are given in the subjoined table.

Four *different sources of* heat were employed in these experiments, dif-*ng in their degrees of intensity*: the naked flame of an oil-lamp; a coil

of platinum wire heated to redness; blackened copper at 734° (390°C); and the same heated to 212° (100°C).

Substances. (Thickness of plate 0·1 inch, nearly.)	Transmission of 100 rays of heat from			
	Oil-lamp.	Red-hot Platinum.	Copper at 734° (390°C).	Copper at 212° (100°C).
Rock-salt, transparent and colourless......	92	92	92	[illegible]
Fluor-spar, colourless........................	78	69	42	[illegible]
Rock-salt, muddy................................	65	65	65	[illegible]
Beryl..	54	23	13	[illegible]
Fluor-spar, greenish	46	88	24	[illegible]
Iceland-spar.......................................	39	28	6	[illegible]
Plate-glass...	39	24	6	[illegible]
Rock-crystal.......................................	38	28	6	[illegible]
Rock-crystal, brown............................	37	28	6	[illegible]
Tourmaline, dark green........................	18	16	3	[illegible]
Citric acid, transparent	11	2	0	[illegible]
Alum, transparent...............................	9	2	0	[illegible]
Sugar-candy	8	0	0	[illegible]
Fluor-spar, green, translucent	8	6	4	[illegible]
Ice, pure and transparent.....................	6	0	0	[illegible]

On examining this remarkable table, which is an abstract of one much more extensive, the first thing that strikes the eye is the want of connection between the power of transmitting heat and that of transmitting light; taking, for instance, the oil-lamp as the source of heat, out of a quantity of heat represented by 100 rays falling upon the pile, the proportion intercepted by similar plates of rock-salt, glass, and alum, may be expressed by the numbers, 8, 61, and 91; and yet these bodies are equally transparent with respect to light. Generally speaking, colour was found to interfere with the transmissive power, but to a very unequal extent; thus, in fluor-spar, colourless, greenish, and deep-green, the quantities transmitted were 78, 46, and 8, while the difference between colourless and brown rock-crystal was only 1. Bodies absolutely opaque, as wood, metals, and black marble, stopped the rays completely, although it was found that the faculty of transmission was possessed to a certain extent by some which were nearly in that condition, as thick plates of brown quartz, black mica, and black glass.

When rays of heat had once passed through a plate of any substance, the interposition of a second similar plate occasioned much less loss than the first; the same thing happened when a number were interposed; the rays, after traversing one plate, being but little interrupted by others of a similar nature.

The next point to be noticed is the great difference in the properties of the rays from different sources. Out of 100 rays from each source which fell on rock-salt, the same proportion was always transmitted, whether the rays proceeded from the intensely heated flame, the red-hot platinum wire, or the copper at 734° (390°C) or 212° (100°C); but this is true of no other substance in the list. In the case of plate-glass, we have the numbers 39, 24, 6, and 0, as representatives of the comparative quantities of heat trans-

mitted through the plate from each source; or in the three varieties of fluor-spar, as below stated:—

	Flame.	Red-heat.	734° (390°C).	212° (100°C).
Colourless	78	69	42	33
Greenish	46	38	24	20
Dark green	8	6	4	3

While one substance, beryl, out of 100 rays from an intensely heated source, suffers 54 to pass, and from the same number (that is, an equal quantity of heat) from metal at 212° (100°C), none at all; another, fluor-spar, transmits rays from the two sources mentioned, in the proportion of 8 to 3.

These, and many other curious phenomena, are fully and completely explained on the supposition, that among the invisible rays of heat differences are to be found exactly analogous to those differences between the rays of light which we are accustomed to call colours. Rock-salt and air are the only substances yet known which are truly *diathermanous*, or equally transparent to all kinds of heat-rays; they are to the latter what white glass or water is to light; they suffer rays of every description to pass with equal facility. All other bodies act like coloured glasses, absorbing certain of the rays more abundantly than the rest, and *colouring*, as it were, the heat which passes through them.

These heat-tints have no direct relation to ordinary colours; their existence is, nevertheless, almost as clearly made out as that of the coloured rays of the spectrum. Bodies at a comparatively low temperature emit rays of such a tint only as to be transmissible by a few substances; as the temperature rises, rays of other heat-colours begin to make their appearance, and transmission of some portion of these rays takes place through a greater number of bodies; while at the temperature of intense ignition we find rays of all colours thrown out, some or other of which will certainly find their way through a great variety of substances.

By cutting rock-salt into prisms and lenses, it is easy to show that radiant heat may be reflected like ordinary light, and its beams made to converge or diverge at pleasure; and, lastly, to complete the analogy, it has been shown to be susceptible of polarization by transmission through plates of doubly-refracting minerals, in the same manner as light itself.[1]

[1] Dr. Forbes, Phil. Mag. for 1835; also M. Melloni, Ann. Chem. et Phys. lxv. 5.

MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface: it is called loadstone, or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished, or even altogether absent. These attractive points, or centres of greatest force, are denominated poles, and the loadstone itself is said to be endued with magnetic polarity.

If one of the poles of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron-filings like the loadstone itself. Farther, the attractive force will be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetised, or to constitute an artificial magnet.

When a magnetised bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a horizontal plane, it is always found to assume a particular direction with regard to the earth, one end pointing nearly north and the other nearly south. If the bar be moved from this position, it will tend to re-assume it, and, after a few oscillations, settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward, as the south pole. A suspended magnet, either natural or artificial, of symmetrical form, serves to exhibit certain phenomena of attraction and repulsion in the presence of a second magnet, which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them; the ends of the bars approach each other, and, if permitted, adhere with considerable force; when, on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetized and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

A piece of iron brought into the neighbourhood of a magnet acquires itself magnetic properties; the intensity of the power thus conferred depends upon that of the magnet and upon the interval which divides the two; becoming greater as that interval decreases, and greatest of all when in actual contact. The iron under these circumstances is said to be magnetized by induction or influence, and the effect, which in an instant reaches its maximum, is at once destroyed by removing the magnet.

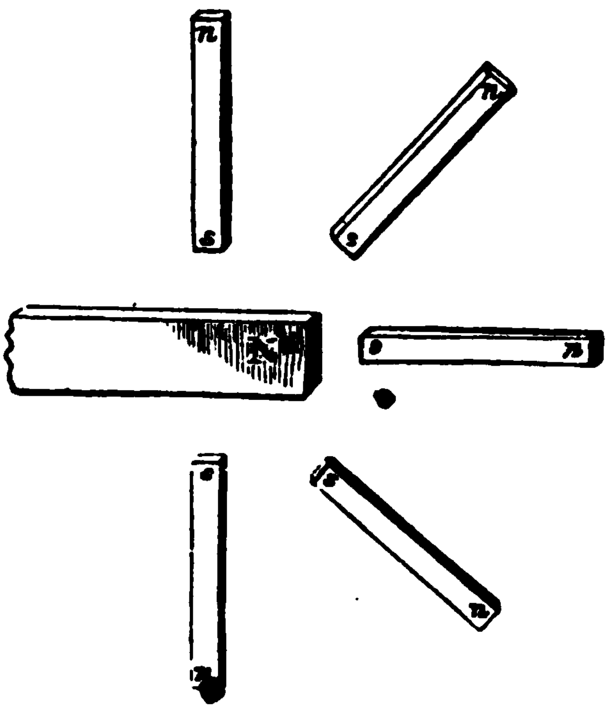
When steel is substituted for iron in this experiment, the inductive action is hardly perceptible at first, and only becomes manifest after the lapse of a certain time; in this condition, when the steel bar is removed from the mag-

t retains a portion of the induced polarity. It becomes, indeed, a per-nt magnet, similar to the first, and retains its peculiar properties for definite period.

particular name is given to this resistance which steel always offers in ater or less degree both to the development of magnetism and its sub-nt destruction; it is called *specific coercive power.*

e rule which regulates the induction of magnetic polarity in all cases eedingly simple, and most important to be remembered. The pole pro-l is always of the opposite name it which produced it, a north pole oping south polarity, and a south north polarity. The north pole of agnet, shown in fig. 60, induces polarity in all the nearer extre-s of the pieces of iron or steel surround it, and a state similar own in all the more remote extre-s. The iron thus magnetized is le of exerting a similar inductive on a second piece, and that upon rd, and so to a great number, the sity of the force diminishing as istance from the permanent mag-ncreases. It is in this way that a et is enabled to hold up a number all pieces of iron, or a bunch of s, each separate piece becoming a et for the time by induction.

Fig. 60.



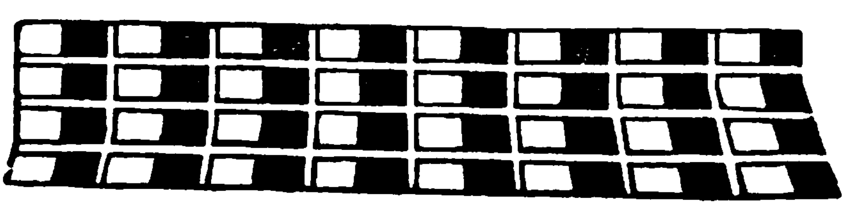
gnetic polarity, similar to that which iron presents, has been found n some of the compounds of iron, in nickel, and in cobalt.

gnetic attractions and repulsions are not in the slightest degree inter-with by the interposition of substances destitute of magnetic proper-Thick plates of glass, shellac, metals, wood, or of any substances t those above mentioned, may be placed between a magnet and a sus-d needle, or a piece of iron under its influence, the distance being pre-l, without the least perceptible alteration in its attractive power, or of induction.

kind of polarity cannot be exhibited without the other. In other , a magnetic pole cannot be insulated. If a magnetized bar of steel oken at its neutral point, or in the middle, each of the broken ends ac-s an opposite pole, so that both portions of the bar become perfect ets; and, if the division be carried still farther, if the bar be broken hundred pieces, each fragment will be a complete magnet, having its north and south poles.

s experiment serves to show very clearly that the apparent polarity of ar is the consequence of the polarity of each individual particle, the of the bar being merely points through which the resultants of all forces pass; the large magnet is made up of an immense number of magnets regularly arranged side by side (fig. 61), all having their north

Fig. 61.



poles looking one way, and their south poles the other. The middle portion of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxta-position with one of an opposite name and of equal power; hence their forces will be exerted in opposite directions and neutralize each other's influence. Such will not be the case at the extremities of the bar; there uncompensated polarity will be found capable of exerting its specific power.

This idea of regular polarization of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small light needles, mounted with an agate cap for suspension upon a fine point; straight bars of various kinds; bars curved into the shape of a horseshoe, &c. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron or keeper, which, becoming magnetized by induction, serves to sustain the polarity of the bar, and even increases in some cases its energy.

The direction spontaneously assumed by a suspended needle indicates that the earth itself has the properties of an enormous magnet, whose south pole is in the northern hemisphere. A line joining the two poles of such a needle or bar indicates the direction of the *magnetic meridian* of the place, which is a vertical plane coincident with the direction of the needle.

The magnetic meridian of a place is not usually coincident with its geographical meridian, but makes with the latter a certain angle called the *declination* of the needle; in other words, the magnetic poles are not situated within the line of the axis of rotation.

The amount of this declination of the needle from the true north and south not only varies at different places, but in the same place is subject to daily, yearly, and secular fluctuations, which are called the variations of declination. Thus, at the commencement of the 17th century, the declination was eastward; in 1660, it was 0; that is, the needle pointed due north and south. Afterwards it became westerly, slowly increasing until the year 1818, when it reached 24° 30′, since which time it has been slowly diminishing.

If a steel bar be supported on a horizontal axis passing exactly through its centre of gravity, it will of course remain equally balanced in any position in which it may happen to be placed; if the bar so adjusted be then magnetized, it will be found to take a permanent direction, the north pole being downwards, and the bar making an angle of about 70°, with a horizontal plane passing through the axis. This is called the *dip*, or *inclination* of the needle, and shows the direction in which the force of terrestrial magnetism is most energetically exerted. The amount of this dip is different in different latitudes; near the equator it is very small, the needle remaining nearly or quite horizontal; as the latitude increases the dip becomes more decided; and over the magnetic pole the bar becomes completely vertical. Such a situation is in fact to be found in the northern hemisphere, considerably to the westward of the geographical pole, in Prince Regent's Inlet. lat. 70° 5′ N. and longitude 96° 46′ W.; the dipping-needle has here been

seen to point directly downwards, while the horizontal or compass-needle ceased to traverse. The position of the south magnetic pole has lately been determined, by the observations of Captain Ross, to be about lat. 73° S. and long. 130° E.

By observing a great number of points near the equator in which the dip becomes reduced to nothing, a line may be traced around the earth, called the magnetic equator, and nearly parallel to this, on both sides, a number of smaller circles, called lines of equal dip. These lines present great irregularities when compared with the equator itself and the parallels of latitude, the magnetic equator deviating from the terrestrial one as much as 12° at its point of greatest divergence. Like the horizontal declination, the dip is also subject to change at the same place. Observations have not yet been made during sufficient time to determine accurately the law and rate of alteration, and great practical difficulties exist also in the construction of the instruments. In the year 1773 it was about 72°; at the present time it is near 69° 5′ in London.

The inductive power of the magnetism of the earth may be shown by holding in a vertical position a bar of very soft iron; the lower end will be found to possess north polarity, and the upper, the contrary state. On reversing the bar the poles are also reversed. All masses of iron whatever, when examined by a suspended needle, will be found in a state of magnetic polarity by the influence of the earth; iron columns, tools in a smith's shop, fire-irons, and other like objects, are all usually magnetic, and those made of steel permanently so. On board ship, the presence of so many large masses of iron, guns, anchors, water-tanks, &c., thus polarized by the earth, causes a derangement of the compass-needles to a very dangerous extent; happily, a plan has been devised for determining the amount of this local attraction in different positions of the ship, and making suitable corrections.

The mariner's compass, which is nothing more than a suspended needle attached to a circular card marked with the points, was not in general use in Europe before the year 1300, although the Chinese have had it from very early antiquity. Its value to the navigator is now very much increased by correct observations of the exact amount of the declination in various parts of the world.

Probably every substance in the world contributes something to the magnetic action of the earth; for, according to the latest discoveries of Mr. Faraday, magnetism is not peculiar to those substances which have more especially been called magnetic, such as iron, nickel, cobalt, but it is the property of all matter, though to a much smaller degree. Very powerful magnets are required to show this remarkable fact. Large horse-shoe magnets, made by the action of the electric current, are most proper. The magnetic action on different substances which are capable of being easily moved, differs not only according to the size, but also according to the nature of the substance. In consequence of this, Faraday divides all bodies into two classes. He calls the one magnetic, or, better, paramagnetic, and the other diamagnetic.

The matter of which a paramagnetic (magnetic) body consists is attracted by both poles of the horse-shoe magnet; on the contrary, the matter of a diamagnetic body is repelled. When a small iron bar is hung by untwisted silk between the poles of the magnet, so that its long diameter can easily move in a horizontal plane, it arranges itself axially, that is, parallel to the straight line which joins the poles, or to the magnetic axis of the poles; assuming at the end which is nearest the north pole, a south pole, and at the end nearest the south pole, a north pole. Whenever the little bar is removed from this position, after a few oscillations, it returns again to its previous position. The whole class of paramagnetic bodies behave in a pre-

cisely similar way under similar circumstances; only in the intensity of the effects great differences occur.

On the contrary, diamagnetic bodies have their long diameters placed equatorially, that is, at right angles to the magnetic axis. They behave, as if at the end opposite to each pole of the magnet, the same kind of polarity existed.

In the first class of substances, besides iron, which is the best representative of the class, we have nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium, aluminium, oxygen, and also most of the compounds of these bodies; most of them, even when in solution. According to Faraday, the following substances are also feebly paramagnetic (magnetic); paper, sealing-wax, indian-ink, porcelain, asbestos, fluor-spar, minium, cinnabar, binoxide of lead, sulphate of zinc, tourmaline, graphite, and charcoal.

In the second class are placed bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, phosphorus, iodine, sulphur, chlorine, hydrogen, and many of their compounds. Also, glass free from iron, water, alcohol, ether, nitric acid, hydrochloric acid, resin, wax, olive oil, oil of turpentine, caoutchouc, sugar, starch, gum, and wood. These are diamagnetic.

If diamagnetic and paramagnetic bodies are combined, their peculiar properties are destroyed. In most of these compounds, occasionally, in consequence of the presence of the smallest quantity of iron, the peculiar magnetic power remains more or less in excess. Thus green bottle glass and many varieties of crown glass are magnetic in consequence of the iron in them.

In order to examine the magnetic properties of fluids they are placed in very thin glass tubes, the ends of which are closed by melting, they are then hung horizontally between the poles of the magnet. Under the influence of poles sufficiently powerful, they begin to swing, and according as the fluid contents are paramagnetic (magnetic), or diamagnetic, they assume an axial or equatorial position.

Under certain circumstances substances which belong to the paramagnetic class behave as if they were diamagnetic. This happens in consequence of a differential action. Thus, for example, when a glass tube full of a dilute solution of sulphate of iron is allowed to swing in a concentrated solution of sulphate of iron, instead of in the air, it assumes an equatorial position. The air, in consequence of the oxygen in it, is itself paramagnetic (magnetic). Hence such bodies as appear to possess feeble diamagnetic properties, can only show their true properties when hung in a vacuum.

Faraday has tried the magnetic condition of gases in different ways. One way consisted in making soap bubbles with the gas which he wished to investigate, and bringing these near the poles. Soap and water alone is feebly diamagnetic. A bubble filled with oxygen was strongly attracted by the magnet. All other gases in the air are diamagnetic, that is, they are repelled. But, as Faraday has shown, in a different way, this partly arises from the paramagnetic (magnetic) property of the air. Thus he found that nitrogen, when this differential action was eliminated, was perfectly indifferent, whether it was condensed or rarified, whether cooled or heated. When the temperature is raised, the diamagnetic property of gases in the air is increased. Hence the flame of a candle or of hydrogen is strongly repelled by the magnet. Even warm air is diamagnetic in cold air.

For some time it has been believed that bodies in a crystalline form had a special and peculiar behaviour when placed between the poles of a magnet. It appeared as though the magnetic directing power of the crystal had some peculiar relation to the position of its optic axis; so that, independently of the magnetic property of the substance of the crystal, if the crystal was

vely optical, it possessed the power of placing its optic axis parallel
he line which joined the poles of the magnet, while optically negative
ls tried to arrange their axes at right angles to this line. This suppo-
is disproved by the excellent investigation of Knoblauch and Tyndall.
ows from their observations that the peculiarity in regard to crystals
pendent on their internal state of cohesion, that is, on unequal com-
on in different directions. If crystalline, or even uncrystalline sub-
s are unequally compressed in different directions, they are found to
s a preponderating directive force in the direction in which they are
strongly compressed, so that when this direction does not coincide with
ng diameter of the body, magnetic bodies will even arrange themselves
orially, and diamagnetic bodies axially.

ELECTRICITY.

If glass, amber, or sealing-wax, be rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper; this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew, and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it; a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented; strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and some of the phenomena of magnetism; the electrical excitement having a twofold nature, like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state. The excited glass and resin being to each other as the north and south poles of a pair of magnetized bars.

To distinguish these two different forms of excitement, terms are employed, which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive; it is customary to call the electricity manifested by glass *positive* or *vitreous*, and that developed in the case of shellac, and bodies of the same class, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface; smooth glass rubbed with silk or wool becomes ordinarily positive, but when ground or roughened by sand or emery, it acquires, under the same circumstances, a negative charge.

The repulsion shown by bodies in the same electrical state is taken advantage of to construct instruments for indicating electrical excitement and pointing out its kind. Two balls of alder-pith (fig. 62), hung by threads or very fine metal wires, serve this purpose in many cases; they open out when excited, in virtue of their mutual repulsion, and show by the degree of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended beneath a bell jar, and communicating with a metal cap above (fig. 63), constitute a much more delicate arrangement, and one of great value in all electrical investigations. These instruments are called electroscopes or electrometers; when excited by the communication of a known kind of electricity, they show, by an increased or diminished divergence, the state of an electrified body brought into their neighbourhood.

Fig. 62.

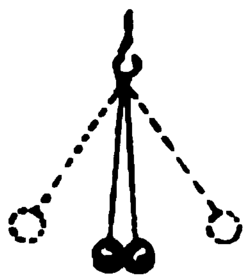
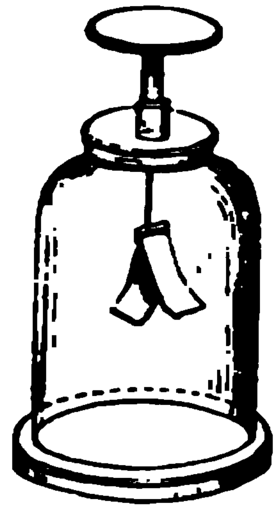


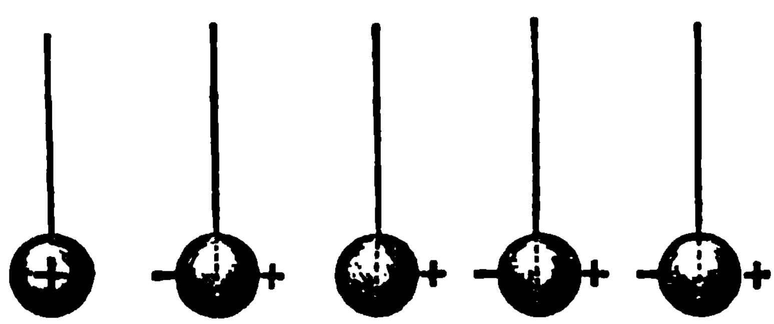
Fig. 63.



One kind of electricity can no more be developed without the other than one kind of magnetism; the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

The induction of magnetism in soft iron has its exact counterpart in electricity; a body already electrified disturbs or polarizes the particles of all surrounding substances in the same manner and according to the same law, inducing a state opposite to its own in the nearer portions, and a similar state in the more remote parts. A series of globes suspended by silk threads, in the manner represented in fig. 64, will each become electric by induction

Fig. 64.



when a charged body is brought near the end of the series, like so many pieces of iron in the vicinity of a magnet, the positive half of each globe looking in one and the same direction, and the negative half in the opposite one. The positive and negative signs are intended to represent the states.

The intensity of the induced electrical disturbance diminishes with the distance from the charged body; if this be removed or discharged, all the effects cease at once.

So far, the greatest resemblance may be traced between these two sets of phenomena; but here it seems in great measure to cease. The magnetic polarity of a piece of steel can awaken polarity in a second piece in contact with it by the act of induction, and in so doing loses nothing whatever of its power; this is an effect completely different from the apparent transfer or discharge of electricity constantly witnessed, which in the air and in liquids often give rise to the appearance of a bright spark of fire. Indeed, ordinary magnetic effects comprise two groups of phenomena only, those namely of attraction and repulsion, and those of induction. But in electricity, in addition to phenomena very closely resembling these, we have the effects of *discharge, to which there is* nothing analogous in magnetism, and *which takes place in an instant* when any electrified body is put in commu

nication with the earth by any one of the class of substances called conductors of electricity; all signs of electrical disturbance then ceasing.

These conductors of electricity, which thus permit discharge to take place through their mass, are contrasted with another class of substances called non-conductors or insulators. The difference, however, is only one of degree, not of kind; the very best conductors offer a certain resistance to the electrical discharge, and the most perfect insulators permit it to a small extent. The metals are by far the best conductors; glass, silk, shellac, and dry gas, or vapour of any sort, the very worst; and between these there are bodies of all degrees of conducting power.

Electrical discharges take place silently and without disturbance in good conductors of sufficient size. But if the charge be very intense, and the conductor very small or imperfect from its nature, it is often destroyed with violence.

When a break is made in a conductor employed in effecting the discharge of a highly-excited body, disruptive or spark-discharge, so well known, takes place across the intervening air, provided the ends of the conductor be not too distant. The electrical spark itself presents many points of interest in the modifications to which it is liable.

The time of transit of the electrical wave through a chain of good conducting bodies of great length is so minute as to be altogether inappreciable to ordinary means of observation. Professor Wheatstone's very ingenious experiments on the subject give, in the instance of motion through a copper wire, a velocity approaching that of light.

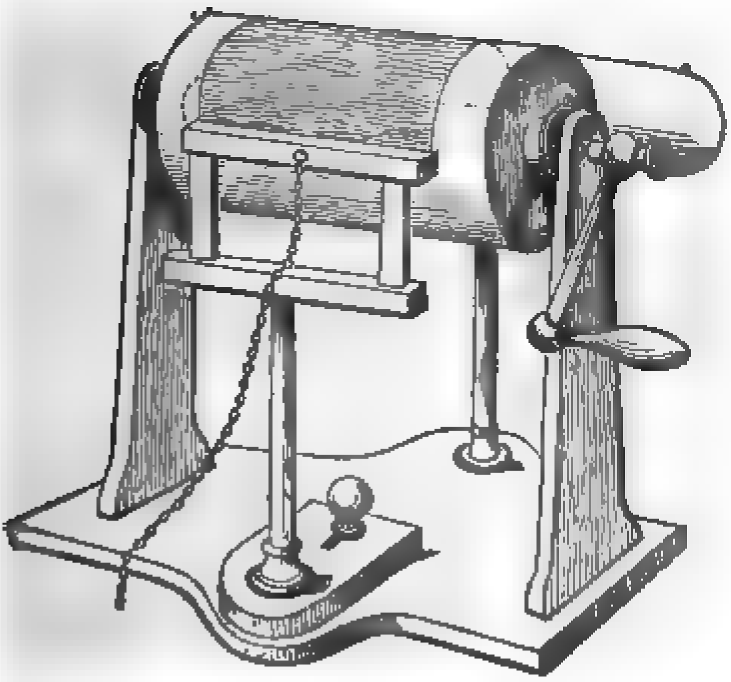
Electrical excitation is *apparent* only upon the surfaces of bodies, or those portions directed towards other objects capable of assuming the opposite state. An insulated ball charged with positive electricity, and placed in the centre of the room, is maintained in that state by the inductive action of the walls of the apartment, which immediately become negatively electrified; in the interior of the ball there is absolutely no electricity to be found, although it may be constructed of open metal gauze, with meshes half an inch wide. Even on the surface the distribution of electrical force will not always be the same; it will depend upon the figure of the body itself, and its position with regard to surrounding objects. The polarity will always be highest in the projecting extremities of the same conducting mass, and greatest of all when these are attenuated to points, in which case the inequality becomes so great that discharge takes place to the air, and the excited condition cannot be maintained.

The construction and use of the common electrical machine, and other pieces of apparatus of great practical utility, will, by the aid of these principles, become intelligible.

A glass cylinder (fig. 65) is mounted with its axis in a horizontal position, and provided with a handle or winch by which it may be turned. A leather cushion is made to press by a spring against one side of the cylinder, while a large metal conducting body, armed with a number of points next the glass, occupies the other; both cushion and conductor are insulated by glass supports, and to the upper edge of the former a piece of silk is attached long enough to reach half round the cylinder. Upon the cushion is spread a quantity of a soft amalgam of tin, zinc, and mercury,[1] mixed up with a little grease; this substance is found by experience to excite glass most powerfully. The cylinder, as it turns, thus becomes charged by friction against the rubber, and as quickly discharged by the row of points attached to the great conductor; and as the latter is also completely insulated, its surface speedily acquires a charge of positive electricity, which may be

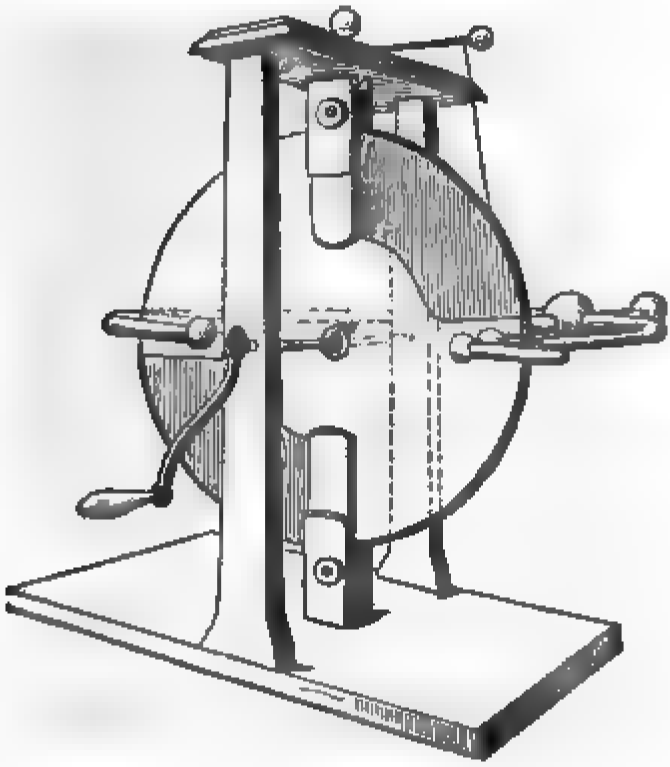
[1] Part tin, 2 zinc, and 6 mercury.

Fig. 65.



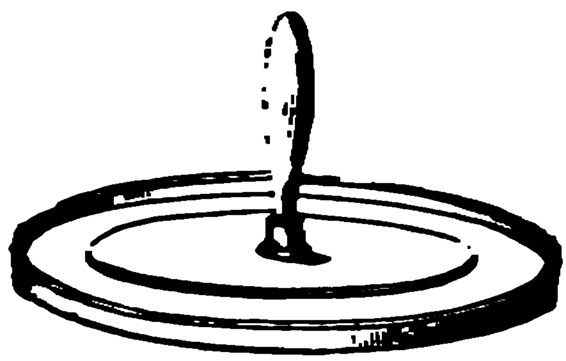
.ted by contact to other insulated bodies. The maximum effect is
/hen the rubber is connected by a chain or wire with the earth.
electricity be wanted, the rubber must be insulated and the con-
harged.
form of the electrical machine consists of a circular plate of glass
oving upon an axis, and provided with two pairs of cushions or

Fig. 66.



The electric spark is often very conveniently employed in chemical inquiries for firing gaseous mixtures in close vessels. A small Leyden jar charged by the machine is the most effective contrivance for this purpose, but not unfrequently, a method may be resorted to which involves less preparation. This is by the use of the electrophorus.

Fig. 68.



A round tray or dish of tinned plate is prepared (fig. 68), having a stout wire round its upper edge; the width may be about twelve inches, and the depth half an inch. This tray is filled with melted shellac, and the surface rendered as even as possible. A brass disc, with rounded edge, of about nine inches diameter, is also provided, and fitted with an insulating handle. When a spark is wanted, the resinous plate is excited by striking with a dry, warm piece of fur, or a silk handkerchief: the cover is placed upon it, and touched by the finger. When the cover is raised, it is found so strongly charged by induction with positive electricity, as to give a bright spark; and, as the resin is not discharged by the cover, which merely touches it at a few points, sparks may be drawn as often as may be wished.

It is not known to what cause the disturbance of the electrical equilibrium of the atmosphere is due: experiment has shown that the higher regions of the air are usually in a positive state, the intensity of which reaches a maximum at a particular period of the day. In cloudy and stormy weather the distribution of the atmospheric electricity becomes much deranged, clouds near the surface of the earth often appearing in a negative state.

The circumstances of a thunder-storm exactly resemble those of the charge and discharge of a coated plate or jar; the cloud and the earth represent the two coatings, and the intervening air the bad-conducting body or *dielectric*. The polarities of the opposed surface and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are capable of conducting freely, the discharge is silent and harmless: but in other cases it often proves highly destructive. These dangerous effects are now in a great measure obviated by the use of lightning-rods attached to buildings, the erection of which, however, demands a number of precautions not always understood or attended to. The masts of ships may be guarded in like manner by metal conductors: Sir W. Snow Harris has devised a most ingenious plan for the purpose, which is now adopted, with the most complete success, in the British Navy.

When two solid conducting bodies are plunged into a liquid which acts upon them unequally, the electric equilibrium is also disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force; the zinc being the metal attacked, becomes negative; and the platinum remaining unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, as when the two surfaces of a coated and charged jar are put into connection.

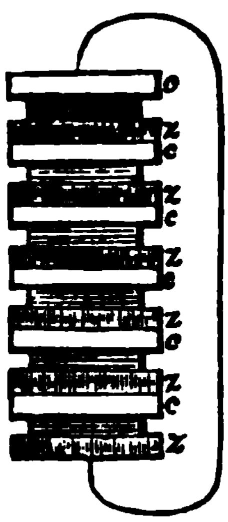
No sooner, however, has this occurred, than the disturbance is repeated, and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary to guard against the idea which the term naturally suggests,

of an actual bodily transfer of something through the substance of the conductors, like water through a pipe; the real nature of all these phenomena is entirely unknown, and may perhaps remain so; the expression is convenient notwithstanding, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and then seeking the nature of the effect from the common meaning of words, may be avoided.

The intensity of the electrical excitement developed by a single pair of metals and a liquid, is too feeble to affect the most delicate gold-leaf electroscope; but, by arranging a number of such alternations in a connected series, in such a manner, that the direction of the current shall be the same in each, the intensity may be very greatly exalted. The two instruments invented by Volta, called the pile, and crown of cups, depend upon this principle.

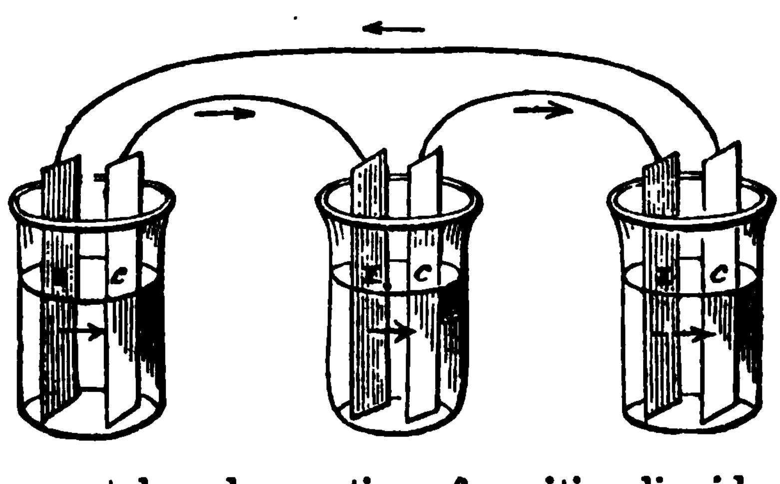
Fig. 69.



Upon a plate of zinc (fig. 69) is laid a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon the zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electric shock will be experienced; but, unlike the momentary effect produced by the discharge of a jar, the sensation will be prolonged and continuous, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states, and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright enduring spark or stream of fire.

The second form of apparatus, or crown of cups, is precisely the same in principle, although different in appearance. A number of cups or glasses (fig. 70) are arranged in a row or circle, each containing a piece of active and

Fig. 70.



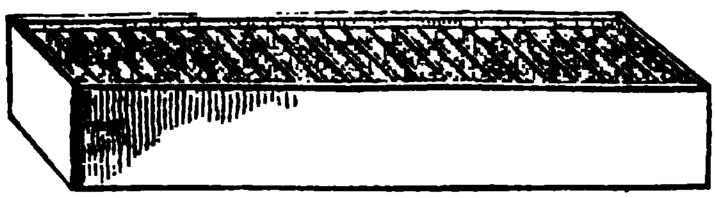
a piece of inactive metal, and a portion of exciting liquid; zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, discharge takes place as before.

When any such electrical arrangement consists merely of a single pair of conductors and an interposed liquid, it is called a simple circuit; when two or more alternations are concerned, the term "compound circuit" is applied; they are called also, indifferently, voltaic batteries. In every form of such

apparatus, however complex it may appear, the direction of the current may be easily understood and remembered. The polarity or disturbance may be considered to commence at the surface of the metal attacked, and to be propagated through the liquid to the inactive conductor, and thence back again by the connecting wire, these extremities of the battery being always respectively negative and positive when the apparatus is insulated. In common parlance, it is said that the current in every battery in an active state starts from the metal attacked, passes through the liquid to the second metal or conducting body, and returns by the wire or other channel of communication; hence, in the pile and crown of cups just described, the current *in* the battery is always from the zinc to the copper; and *out* of the battery, from the copper to the zinc, as shown by the arrows.

In the modification of Volta's original pile, made by Mr. Cruikshank, the zinc and copper plates are soldered together and cemented water-tight into a mahogany trough (fig. 71), which thus becomes divided into a series of

Fig. 71.



cells or compartments capable of receiving the exciting liquid. This apparatus is well fitted to exhibit effects of *tension*, to act upon the electroscope and give shocks; hence its advantageous employment in the application of electricity to medicine, as a very few minutes suffices to prepare it for use. The crown of cups was also put into a much more manageable form by Dr. Babington, and still farther improved, as will hereafter be seen, by Dr. Wollaston. Subsequently, various alterations have been made by different experimenters with a view of obviating certain defects in the common batteries, of which a description will be found towards the middle of this volume.

The term "galvanism," sometimes applied to this branch of electrical science, is used in honour of Professor Galvani, of Bologna, who, in 1790, made the very curious observation that convulsions could be produced in the limbs of a dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions, and although the explanation he offered of the source of the electrical disturbance is no longer generally adopted, his name is very properly associated with the invaluable instrument his genius gave to science.

In the year 1822, Professor Seebeck, of Berlin, discovered another source of electricity, to which allusion has already been made, namely, inequality of temperature and conducting power in different metals placed in contact, or in the same metal in different states of compression and density. Even with a great number of alternations, the current produced is exceedingly feeble compared with that generated by the voltaic pile.

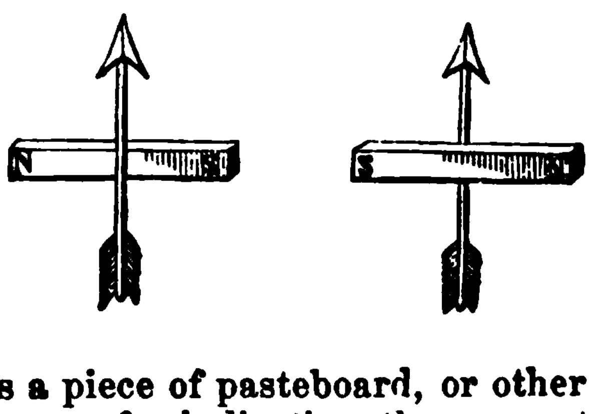
Two or three animals of the class of fishes, as the *torpedo*, or *electric ray*, and the *electric eel* of South America, are furnished with a special organ or apparatus for developing electrical force, which is employed in defence, or in the pursuit of prey. Electricity is here seen to be closely connected with nervous power; the shock is given at the will of the animal, and great exhaustion follows repeated exertion of the power.

Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known. from

the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not until 1819 that the laws of these phenomena were discovered by Professor Œrsted, of Copenhagen, and shortly afterwards fully developed by M. Ampère.

The action which a current of electricity, from whatever source proceeding, exerts upon a magnetized needle is quite peculiar. The poles or centres of magnetic force are neither attracted nor repelled by the wire carrying the current, but made to move *around* the latter, by a force which may be termed *tangential*, and which is exerted in a direction perpendicular at once to that of the current, and to the line joining the pole and the wire. Both poles of the magnet being thus acted upon at the same time, and in contrary directions, the needle is forced to arrange itself across the current, so that its axis, or the line joining the poles, may be perpendicular to the wire; and this is always the position which the needle will assume when the influence of terrestrial magnetism is in any way removed. This curious angular motion may even be shown by suspending a magnet in such a way that one only of its poles shall be subjected to the current; a permanent movement of rotation will continue as long as the current is kept up, its direction being changed by altering the pole, or reversing the current. The moveable connections are made by mercury, into which the points of the conducting-wires dip. It is often of great practical consequence to be able to predict the direction in which a particular pole shall move by a given current, because in all galvanoscopes, and other instruments involving these principles, the movement of the needle is taken as an indication of the direction of the circulating current. And this is easily done by a simple mechanical aid to the memory:—Let the current be supposed to pass through a watch from the face to the back; the motion of the north pole will be in the direction of the hands. Or a little piece of apparatus (fig. 72) may be used if reference is

Fig. 72.

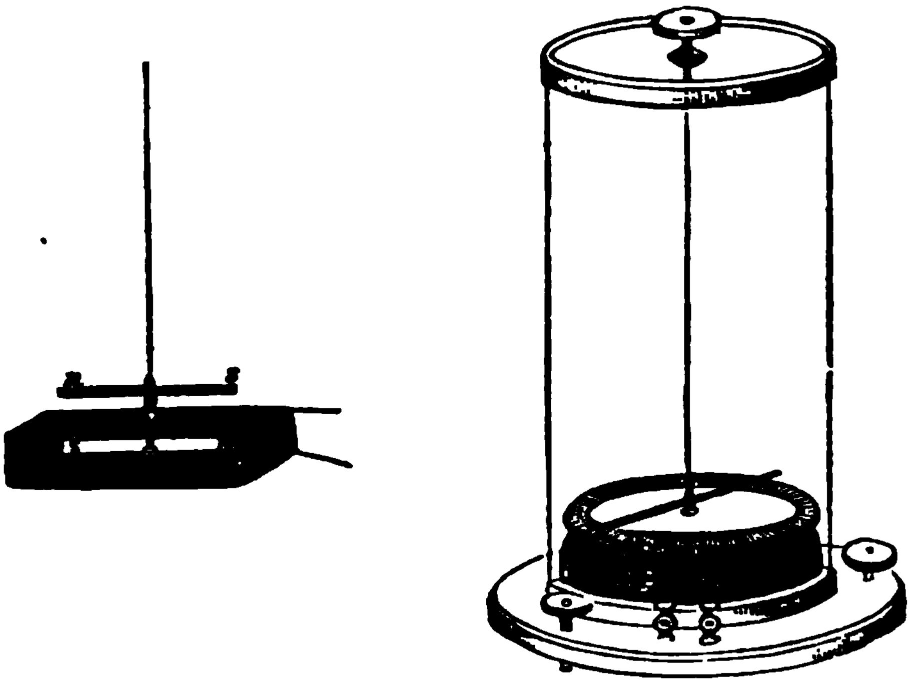


often required; this is a piece of pasteboard, or other suitable material, cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and arranged in the true position with respect to the current. The direction of the latter in the wire of the galvanoscope can at once be known by placing the representative magnet in the direction assumed by the needle itself.

The common galvanoscope, consisting of a coil of wire having a compass-needle suspended on a point within it, is greatly improved by the addition of a second needle, as already in part described, and by a better mode of suspension, a long fibre of silk being used for the purpose. The two needles are of equal size, and magnetized as nearly as possible to the same extent; they are then immovably fixed together, parallel, and with their poles opposed, and hung with the lower needle in the coil and the upper one above it. The advantage gained is twofold; the system is *astatic*, unaffected, or nearly so, by the magnetism of the earth; and the needles being both acted upon in the same manner by the current, are urged with much greater force,

e alone would be, all the actions of every part of the coil being concurrent. A divided circle is placed below the upper needle, by he angular motion can be measured; and the whole is enclosed in shield the needles from the agitation of the air. The arrangement in fig. 73.

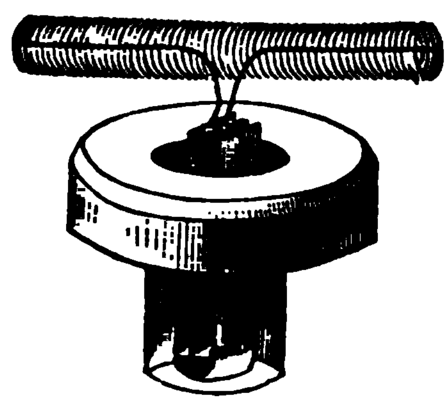
Fig. 73.



ction between the pole and the wire is mutual, as may be shown by g the wire itself moveable and placing a magnet in its vicinity: on ng the circuit, the wire will be put in motion, and, if the arrange-rmits, rotate around the magnetic pole.

e consideration will show, that, from the nature of the electro-dynamic force, a rying a current, bent into a spiral or ust possess the properties of an ordinary ed bar, its extremities being attracted lled by the poles of a magnet. Such is and to be the case, as may be proved by a f arrangements, among which it will be to cite the beautiful little apparatus of r de la Rive.—A short wide glass tube is fixed into a cork ring of considerable ittle voltaic battery, consisting of a single opper and zinc plates, is fitted to the tube, and to these the ends piral are soldered. On filling the tube with dilute acid and floating e in a large basin of water, the helix will be observed to arrange the magnetic meridian, and on trial it will be found to obey a mag-near it in the most perfect manner, as long as the current circu-

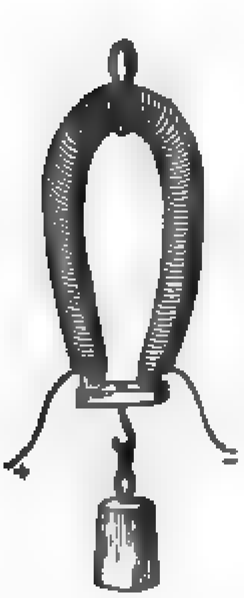
Fig. 74.



an electric current is passed at right angles to a piece of iron or latter acquires magnetic polarity, either temporary or permanent se may be, the direction of the current determining the position of s. This effect is prodigiously increased by causing the current to a number of times round the bar, which then acquires extraordi-gnetic power. A piece of soft iron, worked into the form of a horse-. 75), and surrounded by a coil of copper wire covered with silk or r the purpose of insulation, furnishes an excellent illustration of ctive energy of the current in this respect; when the ends of the

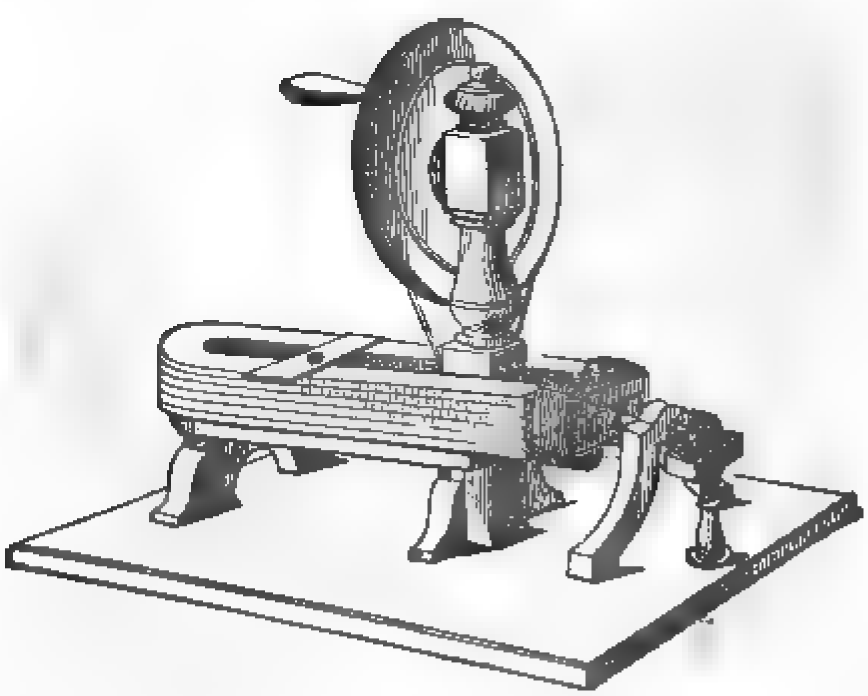
wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

Fig. 75.



A current of electricity can thus develop magnetism in a transverse direction to its own; in the same manner, magnetism can call into activity electric currents. If the two extremities of the coil of the electro-magnet above described be connected with a galvanoscope, and the iron magnetized by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle returning after a few oscillations to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet, so that its induced polarity shall be rapidly reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 76 represents a very powerful arrangement of this kind.

Fig. 76.



When two covered wires are twisted together or laid side by side for some distance, and a current transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction, and on breaking connexion with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. In the same way, when a current of electricity passes through one turn in a coil of wire, it induces two secondary currents in all the other

arms of the coil; when the circuit is closed, the first is moving in the oppo- ite direction to the primary current: the second, when the circuit is broken, as a motion in the same direction as the primary current. The effect of he latter is added to that of the primary current. Hence, if a wire coil be ıade part of the conducting wire of a weak electric pile, and if the primary urrent, by means of an appropriate arrangement, is made and broken in apid succession, we can increase in a remarkable manner the effects which re produced at the moment of breaking the circuit either at the place of ıterruption—such as the spark-discharges; or in secondary closing-con- uctors, such as the action on the nerves or the decomposition of water.

M. Ampère discovered in the course of his investigations a number of xtremely interesting phenomena resulting from the action of electrical cur- ents on each other, which become evident when arrangements are made for iving mobility to the conducting wires. He found that, when two currents lowing in the same direction were made to approach each other, strong ttraction took place between them, and when in opposite directions, an qually strong repulsion.—These effects, which are not difficult to demon- trate, have absolutely no relation that can be traced to ordinary electrical ttractions and repulsions, from which they must be carefully distinguished; hey are purely *dynamic*, having to do with electricity in motion. M. Ampère founded upon this discovery a most beautiful and ingenious hypo- thesis of magnetic actions in general, which explains very clearly the influ- ence of the current upon the needle.

The electricity exhibited under certain peculiar circumstances by a jet of steam, first observed by mere accident, but since closely investigated by Mr. Armstrong, and also by Mr. Faraday, is now referred to the friction, not of the pure steam itself, but of particles of condensed water, against the inte- rior of the exit-tube. It is very doubtful whether *mere evaporation* can cause electrical disturbance, and the hope first entertained that these phenomena would throw light upon the cause of electrical excitement in the atmosphere, is now abandoned. The steam is usually positive, if the jet-pipe be con- structed of wood or clean metal, but the introduction of the smallest trace of oily matter causes a change of sign. The intensity of the charge is, *cæteris paribus*, increased with the elastic force of the steam. By this means, effects have been obtained very far surpassing those of the most powerful plate electrical machines ever constructed.

PART II.

CHEMISTRY OF ELEMENTARY BODIES.

The term *element* or *elementary substance* is applied in chemistry to those forms or modifications of matter which have hitherto resisted all attempts to decompose them. Nothing is ever meant to be affirmed concerning their real nature; they are simply elements to us at the present time; hereafter, by new methods of research, or by new combinations of those already possessed by science, many of the substances which now figure as elements may possibly be shown to be compounds; this has already happened, and may again take place.

The elementary bodies, at present recognised, amount to sixty-two in number; of these, about forty-seven belong to the class of metals. Several of these are of recent discovery and as yet very imperfectly known. The distinction between metals and non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, since the two classes graduate into each other in the most complete manner.

It will be proper to commence with the latter and least numerous division. The elements are named as in the subjoined table, which, however, does not indicate the order in which they will be discussed.

Non-metallic Elements.	Metals.		
Oxygen	Antimony	Gold	Barium
Hydrogen	Chromium	Aluminium	Strontium
Nitrogen	Vanadium	Beryllium	Calcium
Chlorine	Tungsten	(or Glucinum)	Magnesium
Iodine	(or Wolfram)	Zirconium	Zinc
Bromine	Molybdenum	*Norium*	Cadmium
Fluorine	Tantalum	Thorium	Nickel
Carbon	(or Columbium)	Yttrium	Cobalt
Silicon	*Niobium*	Cerium	Copper
Boron	*Pelopium*	*Erbium*	Iron
Sulphur	Titanium	*Terbium*	Manganese
Selenium	Uranium	*Lantanum*	Lithium
Phosphorus	Platinum	*Didymium*	Sodium
——	Palladium	Bismuth	Potassium
Elements of intermediate characters.	Rhodium	Tin	
	Iridium	Mercury	
Arsenic	*Ruthenium*	Silver	
Tellurium	Osmium	Lead	

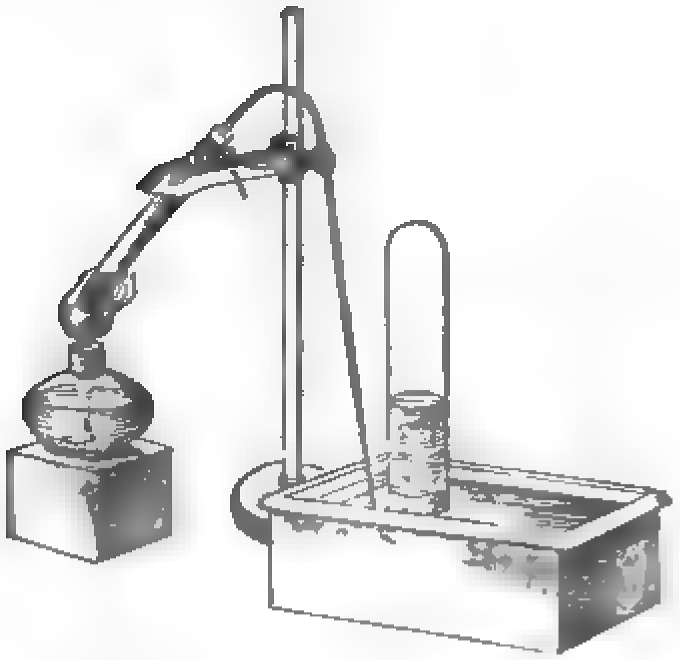
OXYGEN.

er plan of classification, founded on the natural relations of the be adopted, in the practical study of chemistry, it will always be st advantageous to commence with the consideration of the great nts of the ocean and the atmosphere.

was discovered in the year 1774, by Scheele, in Sweden, and Dr. , in England, independently of each other, and described under the *yreal air* and *dephlogisticated air*. The name oxygen[1] was given to oisier some time afterwards. Oxygen exists in a free and uncomte in the atmosphere, mingled with another gaseous body, nitrogen: lirect means exist, however, for separating it from the latter, and, ly, it is always obtained for purposes of experiment by decomrtain of its compounds, which are very numerous.

d oxide of mercury, or *red precipitate* of the old writers, may be with this view. In this substance, the attraction which holds to- mercury and the oxygen is so feeble, that simple exposure to heat bring about decomposition. The red precipitate is placed in a of hard glass, to which is fitted a perforated cork, furnished with narrow glass tube, bent as in the figure. The heat of a spiritng applied to the substance, decomposition speedily commences, of metallic mercury collect in the cool part of the wide tube, which he purpose of a retort, while gas issues in considerable quantity from atus. This gas is collected and examined by the aid of the pneugh, which consists of a vessel of water provided with a shelf, upon nd the jars or bottles destined to receive the gas, filled with water ted. By keeping the level of the liquid above the mouth of the jar, is retained in the latter by the pressure of the atmosphere, and of air is prevented. When brought over the extremity of the gas tube, the bubbles of gas rising through the water collect in the t of the jar and displace the liquid. As soon as one jar is filled,

Fig. 77.



[1] From ὀξύς, acid, and γεννάω, I give rise to.

it may be removed, still keeping its mouth below the water-level, and another substituted. The whole arrangement is shown in fig. 77.

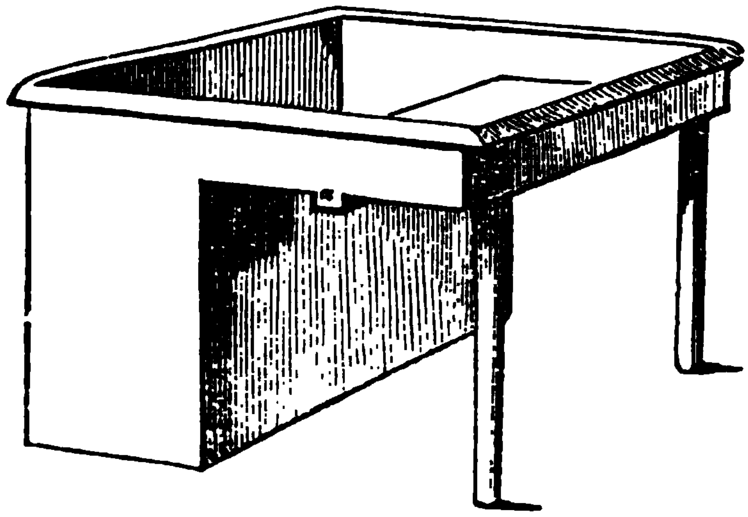
The experiment described is more instructive as an excellent case of the resolution by simple means of a compound body into its constituents, than valuable as a source of oxygen gas. A better and more economical method is to expose to heat in a retort, or flask furnished with a bent tube, a portion of the salt called chlorate of potassa. A common Florence flask serves perfectly well, the heat of a spirit-lamp being sufficient. The salt melts and decomposes with ebullition, yielding a very large quantity of oxygen gas, which may be collected in the way above described. The first portion of the gas often contains a little chlorine. The white saline residue in the flask is chloride of potassium. This plan, which is very easy of execution, is always adopted when very pure gas is required for analytical purpose.

A third method, very good when perfect purity is not demanded, is to heat to redness, in an iron retort or gun-barrel, the black oxide of manganese of commerce, which under these circumstances suffers decomposition, although not to the extent manifest in the red precipitate.

If a little of the black oxide of manganese be finely powdered and mixed with chlorate of potassa, and this mixture heated in a flask or retort by a lamp, oxygen will be disengaged with the utmost facility, and at a far lower temperature than when the chlorate alone is used. All the oxygen comes from the chlorate, the manganese remaining quite unaltered. The materials should be well dried in a capsule before their introduction into the flask. This experiment affords an instance of an effect by no means rare, in which a body seems to act by its mere presence, without taking any obvious part in the change brought about.

Whatever method be chosen—and the same remark applies to the collection of all other gases by similar means—the first portions of gas must be suffered to escape, or be received apart, as they are contaminated by the atmospheric air of the apparatus. The practical management of gases is a point of great importance to the chemical student, and one with which he must endeavour to familiarize himself. The water-trough just described is one of the most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted upon by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made about half an inch in width, and the same in depth, to admit the extremity of the delivery-tube beneath the jar, which stands securely upon the shelf.

Fig. 78.

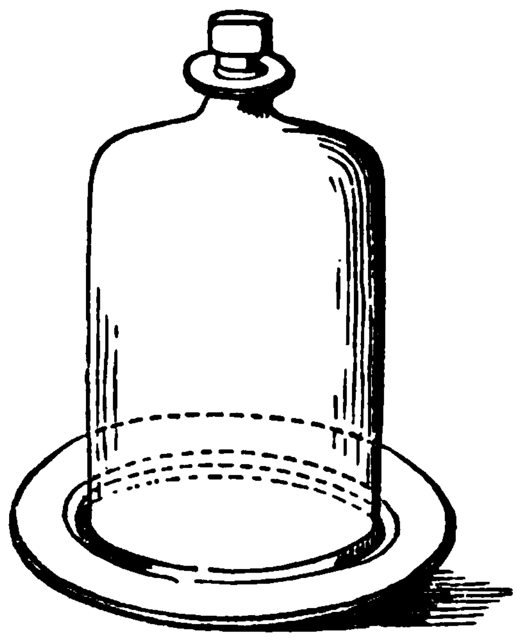


pneumatic trough is required of tolerably large dimensions, it may at advantage have the form and disposition represented in the cut one end of the groove spoken of, which crosses the shelf or shallow s shown at *a*.

are transferred from jar to jar with the utmost facility, by first vessel into which the gas is to be passed with water, inverting it, retaining its mouth below the water-level, and then bringing be- the aperture of the jar containing the gas. On gently inclining the e gas passes by a kind of inverted decantation into the second When the latter is narrow, a funnel may be placed loosely in its which loss of gas will be found to be prevented.

wholly or partially filled with gas at the pneumatic trough may b by placing beneath it a shallow basin, a common plate (fig. 79), so as to ay enough water to cover the edge of and gas, especially oxygen, may be ved for many hours without material

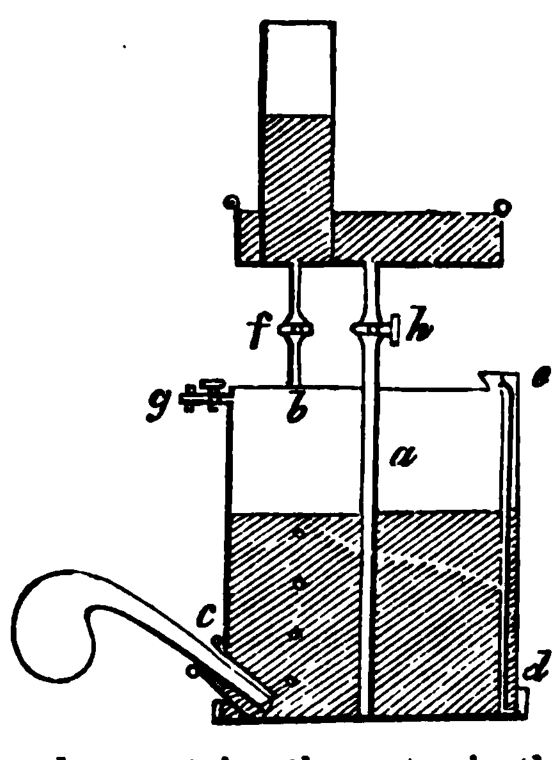
Fig. 79.



s are often capped at the top, and h a stop-cock for transferring to blad- outchouc bags. When such a vessel filled with water, it may be slowly n upright position in the well of the c trough, the stop-cock being open to air to escape, until the water reaches cap. The cock is then to be turned, ar lifted upon the shelf and filled with ie usual way. If the trough be not ugh for this manœuvre, the mouth pplied to the stop-cock, and the vessel sucking out the air until the water rises to the cap. In all cases it to avoid as much as possible wetting the stop-cocks, and other brass s.

pys contrived some years ago an admirable piece of apparatus for nd retaining large quantities of gas. ts of a drum or reservoir of sheet ig. 80), surmounted by a shallow r cistern, the communication be- e two being made by a couple of , furnished with cocks, *f h*, one of sses nearly to the bottom of the shown in the sectional sketch. A e open tube, *c*, is inserted obliquely bottom of the vessel, into which a be tightly screwed. A stop-cock, ie top, serves to transfer gas to a r tube apparatus. A glass water- e, affixed to the side of the drum, nunicating with both top and bot- cates the level of the liquid within. the gas-holder, the plug is first to d into the lower opening, and the mpletely filled with water. All -cocks are then to be closed, and removed. The pressure of the atmosphere retains the water in the r, and if no air-leakage occur, the escape of water is inconsider-

Fig. 80.



able. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn, and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighbouring tube, the hydrostatic pressure of the column of water will cause condensation of the gas, and increase its elastic force, so that on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and be removed without difficulty.

Oxygen, when free or uncombined, is only known in the gaseous state, all attempts to reduce it to the liquid or solid condition by cold and pressure having completely failed. It is, when pure, colourless, tasteless, and inodorous; it is the sustaining principle of animal life, and of all the ordinary phenomena of combustion

Bodies which burn in the air burn with greatly increased splendour in oxygen gas. If a taper be blown out, and then introduced while the wick remains red-hot, it is instantly rekindled: a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the goodness of the gas when it is about to be collected from the retort, or when it has stood some time in contact with water exposed to air.

When a bit of charcoal is affixed to a wire, and plunged with a single point red-hot into a jar of oxygen, it burns with great brilliancy, throwing off beautiful scintillations, until, if the oxygen be in excess, it is completely consumed. An iron wire, or, still better, a steel watch-spring, armed at its extremity with a bit of lighted amadou, and introduced into a vessel of good gas, exhibits a most beautiful appearance of combustion. If the experiment be made in a jar standing on a plate, the fused globules of black oxide of iron fix themselves in the glaze of the latter, after falling through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen, and phosphorus, under similar circumstances, exhibits a splendour which the eye is unable to support.

In these and many other similar cases which might be mentioned, the same ultimate effect is produced as in atmospheric air; the action is, however, more energetic from the absence of the gas which in the air dilutes the oxygen, and enfeebles its chemical powers. The process of respiration in animals is an effect of the same nature as common combustion. The blood contains substances which slowly burn by the aid of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

Oxygen is, bulk for bulk, a little heavier than atmospheric air, which is usually taken as the standard of unity of specific gravity among gases. Its specific gravity is expressed by the number 1·1057;[1] 100 cubic inches at 60° (15°·5C). and under the mean pressure of the atmosphere, that is, 30 inches of mercury, weigh 34·29 grains.

It has been already remarked, that to determine with the last degree of accuracy the specific gravity of a gas, is an operation of very great practical difficulty, but at the same time of very great importance. There are several

[1] Dumas, Ann. Chim. et Phys., 3d series, iii. 275.

methods which may be adopted for this purpose: the one below described appears, on the whole, to be the simplest and best. It requires, however, the most scrupulous care, and the observance of a number of minute precautions, which are absolutely indispensable to success.

The plan of the operation is as follows: A large glass globe is to be filled with the gas to be examined, in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is to be weighed. It is then to be exhausted at the air-pump as far as convenient, and again weighed. Lastly, it is to be filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by a small but excellent stop-cock. A delicate thermometer should be placed in the inside of the globe, secured to the cap. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere: and this is an advantage, since by opening the stop-cock for a single instant when the globe has attained an equilibrium of temperature, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should sensibly vary during the time occupied by the experiment. It is hardly necessary to remark, that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air as nearly as possible to the same temperature, to obviate the necessity of a correction, or at least to diminish almost to nothing the errors involved by such a process.

The compounds formed by the direct union of oxygen with other bodies, bear the general name of oxides; these are very numerous and important. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations, potassa, soda, or the oxide of silver or of lead; these are denominated *alkaline* or *basic* oxides, or sometimes *salifiable bases*. The oxides of the second group have properties exactly opposed to those of the bodies mentioned; oil of vitriol and phosphoric acid may be taken as the types or representatives of the class: they are called *acids*, and tend strongly to unite with the basic oxides. When this happens, what is called a *salt* is generated as sulphate of potassa, or phosphate of silver, each of these substances being compounded of a pair of oxides, one of which is highly basic and the other highly acid.

Then there remains a third group of what may be termed *neutral* oxides, from their little disposition to enter into combination. The black oxide of manganese, already mentioned, is an excellent example.

It very frequently happens that a body is capable of uniting with oxygen in several proportions, forming a series of oxides, to which it is necessary to give distinguishing names. The rule in such cases is very simple, at least when the oxides of the metals are concerned. In such a series it is always found that one out of the number has a strongly-marked basic character; to this the term *protoxide* is given. The compounds next succeeding receive the names of *binoxide* or *deutoxide*, *teroxide* or *tritoxide*, &c., from the Latin or Greek numerals, the different grades of oxidation being thus indicated. If

there be a compound between the protoxide and binoxide, the name *sesqui-oxide* is usually applied. So it is usual to call the highest oxide, not having distinctly acid characters, *peroxide*, from the Latin prefix, signifying excess. Any compound containing less oxygen than the protoxide, is called a *sub-oxide*. *Superoxide* or *hyperoxide* are words sometimes used instead of peroxide.

Ozone.—It has long been known that dry oxygen, or atmospheric air, when exposed to the passage of a series of electric sparks, emits a peculiar and somewhat metallic odour. The same odour may be imparted to moist oxygen, by allowing phosphorus to remain for some time in it. A more accurate examination of this odorous air has shown that, in addition to the smell, it assumes several properties not exhibited by pure oxygen. One of its most curious effects is the liberation of iodine from iodide of potassium. The oxygen thus altered has been the subject of many researches lately, particularly by Prof. Schoenbein, of Basel, who proposed the name of ozone[1] for it. The true nature of ozone, however, is still unknown, most probably it is a peculiar modification of oxygen.

HYDROGEN.

Hydrogen is always obtained for experimental purposes by deoxidizing water, of which it forms the characteristic component.[2]

If a tube of iron or porcelain, containing a quantity of filings or turnings of iron, be fixed across a furnace, and its middle portion be made red-hot, and then the vapour of water transmitted over the heated metal, a large quantity of permanent gas will be disengaged from the tube, and the iron will become converted into oxide, and acquire an increase in weight. The gas is hydrogen; it may be collected over water and examined.

When zinc is put into water, chemical action of the liquid upon the metal is imperceptible; but if a little sulphuric acid be added, decomposition of the water ensues, the oxygen unites with the zinc, forming oxide of zinc, which is instantly dissolved by the acid, while the hydrogen, previously in union with the oxygen, is disengaged in the gaseous form. The reaction is represented in the subjoined diagram.

Water { Hydrogen ———————— Free.
Water { Oxygen ——
Zinc ———————— oxide of zinc } Sulphate of
Sulphuric acid ———————— } oxide of zinc.

It is not easy to explain the fact of the ready decomposition of water by zinc, in presence of an acid or other substance which can unite with the oxide so produced; it is, however, a kind of reaction of very common occurrence in chemistry.

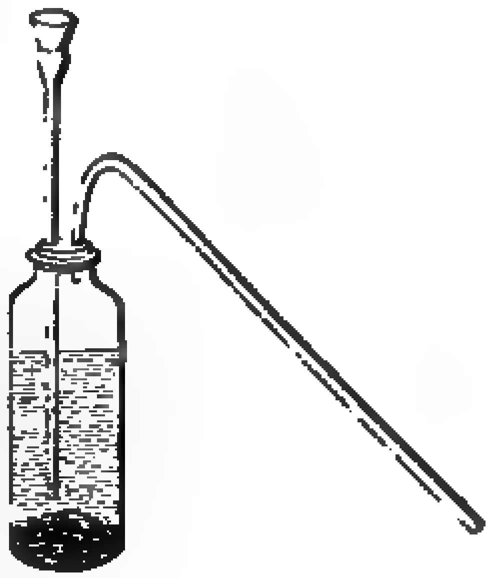
The simplest method of preparing the gas is the following.—A wide-necked bottle is chosen, and fitted with a sound cork (fig. 81). perforated by two holes for the reception of a small tube-funnel reaching nearly to the bottom of the bottle, and a piece of bent glass tube to convey away the disengaged gas. Granulated zinc, or scraps of the malleable metal, are put into the bottle, together with a little water, and sulphuric acid slowly added by the funnel, the point of which should dip into the liquid. The evolution of gas is easily regulated by the supply of acid, and when enough has been discharged to expel the air of the vessel, it may be collected over water into a jar, or passed into a gas-holder. In the absence of zinc, filings of iron or small nails may be used, but with less advantage.

[1] From ὄζω, I smell.

[2] Hence the name, from ὕδωρ, water, and γεννάω.

practice will soon enable the ... construct and arrange a variety ... forms of apparatus, in which ... d other articles always at ... made to supersede more ... ruments. Glass tube, pur-... weight of the maker, may be ... atching with a file, and then ... little force with both hands. ... softened and bent, when of ... ensions, by the flame of a ..., or even a candle or gas-jet. ... be perforated by a heated ... he hole rendered smooth and ... by a round file, or the in-... rk-borer of Dr. Mohr, now ... of most instrument makers, ... sed instead. Lastly, in the ... ad fitting, or unsoundness in ... itself, a little yellow wax ... er the surface, or even a little grease applied with the finger, ... sound and air-tight, when not exposed to heat.

Fig. 51.

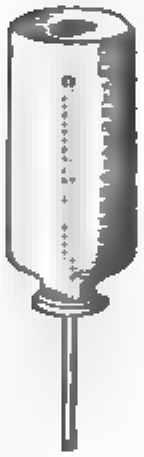


... n is colourless, tasteless, and inodorous, when quite pure. To ... this condition, it must be prepared from the purest zinc that can ... l, and passed in succession through solutions of potassa and nitrate ... When prepared from commercial zinc, it has a slight smell, which ... mpurity, and when iron has been used, the odour becomes very ... disagreeable. It is inflammable, burning when kindled with a ... vish flame, and evolving much heat, but very little light. The ... he combustion is water. It is even less soluble in water than ... d has never been liquefied. Although destitute of poisonous pro-... is incapable of sustaining life.

... of specific gravity, hydrogen is the lightest substance known; ... 1 Boussingault place its density between 0·0691 and ... ence 100 cubic inches will weigh, under ordinary ... ces of pressure and temperature, 2·14 grains.

... gas is much lighter or much heavier than atmospheric ... often be collected and examined without the aid of ... atic trough. A bottle or narrow jar may be filled ... gen without much admixture of air, by inverting it ... xtremity of an upright tube delivering the gas (fig. ... short time, if the supply be copious, the air will ... displaced and the vessel filled. It may now be ... he vertical position being carefully retained, and ... stopper or glass plate. If the mouth of the jar be ... must be partially closed by a piece of card-board ... operation. This method of collecting gases by ... nt is often extremely useful. Hydrogen was for-... for filling air-balloons, being made for the purpose ... from zinc or iron and dilute sulphuric acid. Its use ... erseded by that of coal-gas, which may be made very light by ... a high temperature in the manufacture. Although far inferior ... drogen in buoyant power, it is found in practice to possess advan-... that substance, while its greater density is easily compensated ... ng the magnitude of the balloon.

Fig. 52.



[1] Ann. Chim. et Phys. 3d. series, viii. 201.

There is a very remarkable property enjoyed by gases and vapours in general, which is seen in a high degree of intensity in the case of hydrogen, this is what is called *diffusive power.* If two bottles, containing gases which do not act chemically upon each other at common temperatures, be connected by a narrow tube and left for some time, these will be found, at the expiration of a certain period, depending much upon the narrowness of the tube and its length, uniformly mixed, even though the gases differ greatly in density, and the system has been arranged in a vertical position, with the heaviest gas downwards. Oxygen and hydrogen can thus be made to mix, in a few hours, against the action of gravity, through a tube a yard in length, and not more than one-quarter of an inch in diameter; and the fact is true of all other gases which are destitute of direct action upon each other.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices with the same degree of facility. Professor Graham, to whom we are indebted for a very valuable investigation of this interesting subject, has established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the diffusive power varies inversely as the square root of the density of the gas itself. Thus, in the experiment supposed, if one half of the vessel be filled with hydrogen and the other half with oxygen, the two gases will penetrate the diaphragm at very different rates; four cubic inches of hydrogen will pass into the oxygen side, while one cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of 1 to 16; their relative rates of diffusion will be inversely as the square roots of these numbers, or 4 to 1.

Fig. 83.

By making the diaphragm of some flexible material, as a piece of membrane, the accumulation of the lighter gas on the side of the heavier may be rendered evident by the bulging of the membrane. The simplest and most striking method of making the experiment is by the use of Professor Graham's diffusion-tube (fig. 83). This is merely a piece of wide glass tube ten or twelve inches in length, having one of its extremities closed by a plate of plaster of Paris about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly, that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air.

It is impossible to over-estimate the importance in the great economy of Nature, of this very curious law affecting the constitution of gaseous bodies; it is the principal means by which the atmosphere is preserved in an uniform state, and the accumulation of poisonous gases and exhalations in towns and other confined localities prevented.

A distinction must be carefully drawn between real diffusion through small apertures, and the apparently similar passage of gas through wet or moist membranes and other substances, which is really due to temporary liquefaction or solution of the gas, and is an effect completely different from diffusion, properly so called. For example, the diffusive power of carbonic acid

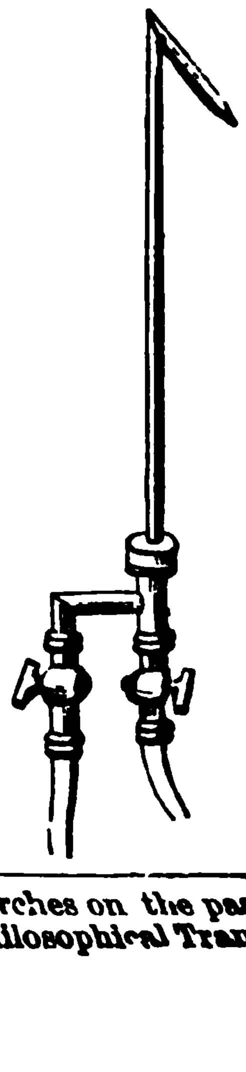
ıospheric air is very small, but it passes into the latter through a wet with the utmost ease, in virtue of its solubility in the water with ıe membrane is moistened. It is by such a process that the function iration is performed; the aëration of the blood in the lungs, and the gement of the carbonic acid, are effected through wet membranes; ɔd is never brought into actual contact with the air, but receives its of oxygen, and disembarrasses itself of carbonic acid by this kind ious diffusion.

ıigh diffusive power of hydrogen against air renders it impossible to hat gas for any length of time in a bladder or caoutchouc bag: it is safe to keep it long in a gas-holder, lest it should become mixed with light accidental leakage, and be rendered explosive.[1]

s been stated, that, although the light emitted by the flame of pure ɜn is exceedingly feeble, yet the temperature of the flame is very This temperature may be still farther exalted by previously mixing rogen with as much oxygen as it requires for combination, that is, presently be seen, exactly half its volume. Such a mixture burns npowder, independently of the external air. When raised to the e temperature for combination, the two gases unite with explosive). If a strong bottle, holding not more than half a pint, be filled ıch a mixture, the introduction of a lighted match or red-hot wire nes in a moment the union of the gases. By certain precautions, a ı of oxygen and hydrogen can be burned at a jet without communi- ıf fire to the contents of the vessel; the flame is in this case *solid.*

:le consideration will show, that all ordinary flames burning in the ı pure oxygen are, of necessity, hollow. The act of combustion is more than the energetic union of the substance burned with the ding oxygen; and this union can only take place at the surface of ning body. Such is not the case, however, with the flame now under ration; the combustible and the oxygen are already mixed, and only to have their temperature a little raised to cause them to combine in art. The flame so produced is very different in phy- aracters from that of a simple jet of hydrogen or any ombustible gas; it is long and pointed, and very re- le in appearance.

Fig. 84.



afety-jet of Mr. Hemming, the construction of which ı a principle not yet discussed, may be adapted to a com- ıdder containing the mixture, and held under the arm, ɜ gas forced through the jet by a little pressure. ;h the jet, properly constructed, is believed to be safe, t to use nothing stronger than a bladder, for fear of ı the event of an explosion. The gases are often con- n separate reservoirs, a pair of large gas-holders, for), and only suffered to mix in the jet itself, as in the ınce of Professor Daniell; in this way all danger is . The eye speedily becomes accustomed to the pecu- pearance of the true hydro-oxygen flame, so as to the supply of each gas to be exactly regulated by stop-cocks attached to the jet (fig. 84).

ce of thick platinum wire introduced into the flame ıydro-oxygen blowpipe melts with the greatest ease; ı-spring or small steel file burns with the utmost :y, throwing off showers of beautiful sparks; an in-

[1] ssor Graham has since published a very extensive series of researches on the pas- ıses through *narrow tubes, which will* be found in detail in the Philosophical Trans- r *1846, p. 573.*

combustible oxidized body, as magnesia or lime, becomes so intensely ignited, as to glow with a light insupportable to the eye, and to be susceptible of employment as a most powerful illuminator, as a substitute for the sun's rays in the solar microscope, and for night-signals in trigonometrical surveys.

Fig. 85.

If a long glass tube, open at both ends, be held over a jet of hydrogen (fig. 85), a series of musical sounds are sometimes produced by the partial extinction and rekindling of the flame by the ascending current of air. These little explosions succeed each other at regular intervals, and so rapidly as to give rise to a musical note, the pitch depending chiefly upon the length and diameter of the tube.

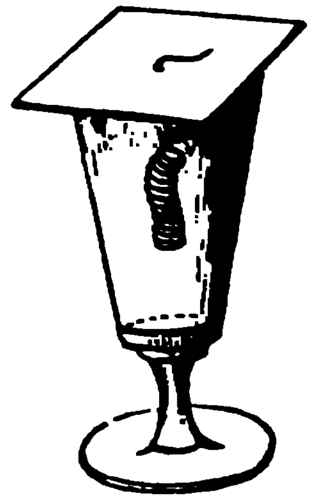
Although oxygen and hydrogen may be kept mixed at common temperatures for any length of time without combination taking place, yet, under particular circumstances, they unite quietly and without explosion. Some years ago, Professor Döbereiner, of Jena, made the curious observation, that finely-divided platinum possessed the power of determining the union of the gases; and, more recently, Mr. Faraday has shown that the state of minute division is by no means indispensable, since rolled plates of the metal had the same property, provided their surfaces were absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, enjoy the same property, although to a far inferior degree, since they often require to be aided by a little heat. When a piece of platinum foil, which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, the platinum becoming so hot, that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and exceedingly clean, and the gases very pure, then its temperature rises after a time to actual redness, and the residue of the mixture explodes. But this is an effect altogether accidental, and dependent upon the high temperature of the platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or hydrogen and air; a jet of hydrogen thrown upon a little of the spongy metal, contained in a glass or capsule, becomes at once kindled, and on this principle machines for the production of instantaneous light have been constructed. These, however, only act well when constantly used; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects, is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces, and that this faculty is enjoyed pre-eminently by certain of the non-oxidizable metals, as platinum and gold. Oxygen and hydrogen may thus, under these circumstances, be brought, as it were, within the sphere of their mutual attractions by a temporary increase of density, whereupon combination ensues.

Coal-gas and ether or alcohol vapour may be made to exhibit the phenomenon of quiet oxidation under the influence of this remarkable surface-action. A close spiral of slender platinum wire, a roll of thin foil, or even a common platinum crucible, heated to dull redness, and then held in a jet of coal-gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white-hot, and then the gas takes fire.

A very pleasing experiment may be made by attaching such a coil of wire to a card, and suspending it in a glass containing a few drops of ether (fig. 86), having previously made it red-hot in the flame of a spirit-lamp. The wire continues to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapour which attacks the eyes. The combustion of the ether is in this case but partial; a portion of its hydrogen is alone removed, and the whole of the carbon left untouched.

Fig. 86.



A coil of thin platinum wire may be placed over the wick of a spirit-lamp, or a ball of spongy platinum sustained just above the cotton; on lighting the lamp, and then blowing it out as soon as the metal appears red-hot, slow combustion of the spirit drawn up by the capillarity of the wick will take place, accompanied by the pungent vapours just mentioned, which may be modified, and even rendered agreeable, by dissolving in the liquid some sweet-smelling essential oil or resin.

Hydrogen forms numerous compounds with other bodies, although it is greatly surpassed in this respect not only by oxygen, but by many of the other elements. The chemical relations of hydrogen tend to place it beside the metals. The great discrepancy in physical properties is perhaps more apparent than real. Hydrogen is yet unknown in the solid condition, while, on the other hand, the vapour of the metal mercury is as transparent and colourless as hydrogen itself. This vapour is only about seven times heavier than atmospheric air, so that the difference in this respect is not nearly so great as that in the other direction between air and hydrogen.

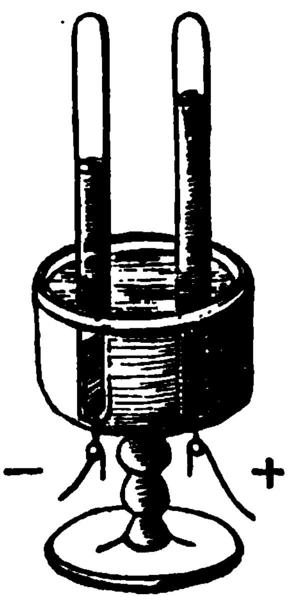
There are two oxides of hydrogen, namely, *water*, and a very peculiar substance, discovered in the year 1818, by M. Thenard, called *binoxide of hydrogen*.

It appears that the composition of water was first demonstrated in the year 1781, by Mr. Cavendish,[1] but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has from time to time to the present day occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry: the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second, but in this particular instance both may be employed, although the results of the synthesis are most valuable.

The most elegant example of analysis of water would probably be found in its decomposition by voltaic electricity. When water is acidulated so as to render it a conductor, and a portion interposed between a pair of platinum plates connected with the extremities of a voltaic apparatus of moderate power, decomposition of the liquid takes place in a very interesting manner; oxygen, in a state of perfect purity, is evolved from the water in contact with the plate belonging to the copper end of the battery, and hydrogen, equally pure, is disengaged at the plate connected with the zinc extremity, the middle portions of liquid remaining apparently unaltered. By placing small graduated jars over the platinum plates, the gases can be

[1] A claim to the discovery of the composition of water on behalf of Mr. James Watt, has been very strongly urged, and supported by such evidence that the reader of the controversy may be led to *the conclusion that the* discovery was made by both parties nearly simultaneously, *and unknown to each other.*

Fig. 87.



collected, and their quantities determined. Fig. 87 will show at a glance the whole arrangement; the conducting wires pass through the bottom of the glass cup, and thence to the battery.

When this experiment has been continued a sufficient time, it will be found that the volume of the hydrogen is a *very* little above twice that of the oxygen; were it not for the accidental circumstance of oxygen being sensibly more soluble in water than hydrogen, the proportion of two to one by measure would come out exactly.

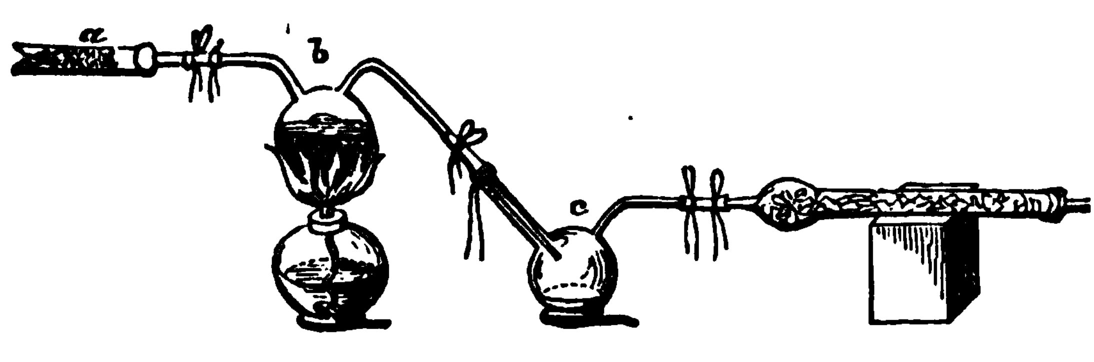
Water, as Mr. Grove has lately shown, is likewise decomposed into its constituents by heat. The effect is produced by introducing platinum balls, ignited by electricity or other means, into water or steam. The two gases are, however, obtained in very small quantities at a time.

Fi

When oxygen and hydrogen, both as pure as possible, are mixed in the proportions mentioned, passed into a strong glass tube filled with mercury, and exploded by the electric spark, all the mixture disappears, and the mercury is forced up into the tube, filling it completely. The same experiment may be made with the explosion-vessel or eudiometer of Mr. Cavendish. (Fig. 88.) The instrument is exhausted at the air-pump, and then filled from a capped jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture, and if the stop-cock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of an imperfect exhaustion.

The process upon which most reliance is placed is that in which pure oxide of copper is reduced at a red heat by hydrogen, and the water so formed collected and weighed. This oxide suffers no change by heat alone, but the momentary contact of hydrogen, or any common combustible matter at a l perature, suffices to reduce a corresponding portion to the meta Fig. 89 will serve to convey some idea of the arrangement adop searches of this kind.

Fig. 89.



A copious supply of hydrogen is procured by the action of d phuric acid upon the purest zinc that can be obtained; the gas i *pass in* succession through solutions of silver and strong caustic p *which its purification* is completed. After this, it is conducted

be three or four feet in length, filled with fragments of pumice-stone steped in concentrated oil of vitriol, or with anhydrous phosphoric acid. These substances have such an extraordinary attraction for aqueous vapour, that they dry the gas completely during its transit. The extremity of this tube is shown at *a*. The dry hydrogen thus arrives at the part of the apparatus containing the oxide of copper, represented at *b*; this consists of a two-necked flask of very hard white glass, maintained at a red heat by a spirit-lamp placed beneath. As the decomposition proceeds, the water produced by the reduction of the oxide begins to condense in the second neck of the flask, whence it drops into the receiver *c*, provided for the purpose. A second desiccating tube prevents the loss of aqueous vapour by the current of gas which passes in excess.

Before the experiment can be commenced, the oxide of copper, the purity of which is well ascertained, must be heated to redness for some time in a current of dry air; it is then suffered to cool, and very carefully weighed with the flask. The empty receiver and second drying tube are also weighed, the disengagement of gas set up, and when the air has been displaced, heat slowly applied to the oxide. The action is at first very energetic; the oxide then exhibits the appearance of ignition; as the decomposition proceeds, it becomes more sluggish, and requires the application of a good deal of heat to effect its completion.

When the process is at an end, and the apparatus perfectly cool, the stream of gas is discontinued, dry air is drawn through the whole arrangement, and, lastly, the parts are disconnected and re-weighed. The loss of the oxide of copper gives the oxygen; the gain of the receiver and its drying-tube indicates the water, and the difference between the two, the hydrogen.

A set of experiments, made in Paris in the year 1820,[1] by MM. Dulong and Berzelius, gave as a mean result for the composition of water by weight, 8·009 parts oxygen to 1 part hydrogen; numbers so nearly in the proportion of 8 to 1, that the latter have usually been assumed to be true.

Quite recently the subject has been re-investigated by M. Dumas,[2] with the most scrupulous precision, and the above supposition fully confirmed. The composition of water may therefore be considered as established: it contains by weight 8 parts oxygen to 1 part hydrogen, and by measure, 1 volume oxygen to 2 volumes hydrogen. The densities of the gases, as already mentioned, correspond very closely with these results.

The physical properties of water are too well known to need lengthened description; it is, when pure, colourless and transparent, destitute of taste and odour, and an exceedingly bad conductor of electricity of low tension. It attains its greatest density towards 40° (4°·5C), freezes at 32° (0°C), and boils under the pressure of the atmosphere at or near 212° (100°C). It evaporates at all temperatures. One cubic inch at 62° (16°·7C) weighs 252·45 grains. It is 815 times heavier than air; an imperial gallon weighs 70,000 grains or 10 lb. avoirdupois. To all ordinary observation, water is incompressible; very accurate experiments have nevertheless shown that it does yield to a small extent when the power employed is very great; the diminution of volume for each atmosphere of pressure being about 51-millionths of the whole.

Clear water, although colourless in small bulk, is blue like the atmosphere when viewed in mass. This is seen in the deep ultramarine tint of the ocean, and perhaps in a still more beautiful manner in the lakes of Switzerland and other Alpine countries, and in the rivers which issue from them; the slightest admixture of mud or suspended impurity destroying the effect.

[1] Ann. Chim. et Phys. xv. 386.
[2] Ann. Chim. et Phys. 3rd series, viii. 189.

The same magnificent colour is visible in the fissures and caverns fou the ice of the glaciers, which is usually extremely pure and transp within, although foul upon the surface.

Steam, or vapour of water, in its state of greatest density at 212° (10 compared with air at the same temperature, and possessing an equal e force, has a specific gravity expressed by the fraction of 0·625. In thi dition, it may be represented as containing, in every two volumes volumes of hydrogen, and one volume of oxygen.

Water seldom or never occurs in nature in a state of perfect purity; the rain which falls in the open country, contains a trace of ammoniacal while rivers and springs are invariably contaminated to a greater o extent with soluble matters, saline and organic. Simple filtration thro porous stone or a bed of sand will separate suspended impurities, bu tillation alone will free the liquid from those that are dissolved. In the paration of distilled water, which is an article of large consumption i scientific laboratory, it is proper to reject the first portions which pass and to avoid carrying the distillation to dryness. The process may be ducted in a metal still furnished with a worm or condenser of silver o lead must not be used.

The ocean is the great recipient of the saline matter carried down b rivers which drain the land; hence the vast accumulation of salts. following table will serve to convey an idea of the ordinary compositi sea-water; the analysis is by Dr. Schweitzer,[1] of Brighton, the water that of the Channel:—

1000 grains contained

Water	964·745
Chloride of sodium	27·059
Chloride of potassium	0·766
Chloride of magnesium	3·666
Bromide of magnesium	0·029
Sulphate of magnesia	2·296
Sulphate of lime	1·406
Carbonate of lime	0·033
Traces of iodine and ammoniacal salt	
	1000·000

Its specific gravity was found to be 1·0274 at 60° (15°·5C).

Sea-water is liable to variations of density and composition by the infl of local causes, such as the proximity of large rivers or masses of m ice, and other circumstances.

Natural springs are often impregnated to a great extent with solubl stances derived from the rocks they traverse; such are the various m waters scattered over the whole earth, and to which medicinal virtu attributed. Some of these hold protoxide of iron in solution, and are vescent from carbonic acid gas; others are alkaline, probably from t sing rocks of volcanic origin; some contain a very notable quantity of or bromine. Their temperatures also are as variable as their che nature. A tabular notice of some of the most remarkable of these v will be found in the Appendix.

Water enters into direct combination with other bodies, forming a of compounds called *hydrates;* the action is often very energetic, mucl being evolved, as in the case of the slaking of lime, which is really th duction of a hydrate of that base. Sometimes the attraction betwee

[1] Phil. Mag. July, 1839.

water and the second body is so great that the compound is not decomposable by any heat that can be applied; the hydrates of potassa and soda, and of phosphoric acid, furnish examples. Oil of vitriol is a hydrate of sulphuric acid, from which the water cannot be thus separated.

Water very frequently combines with saline substances in a less intimate manner than that above described, constituting what is called water of crystallization, from its connexion with the geometrical figure of the salt. In this case it is easily driven off by the application of heat.

Lastly, the solvent properties of water far exceed those of any other liquid known. Among salts, a very large proportion are soluble to a greater or less extent, the solubility usually increasing with the temperature, so that a hot saturated solution deposits crystals on cooling. There are a few exceptions to this law, one of the most remarkable of which is common salt, the solubility of which is nearly the same at all temperatures; the hydrate and certain organic salts of lime, also, dissolve more freely in cold than in hot water.

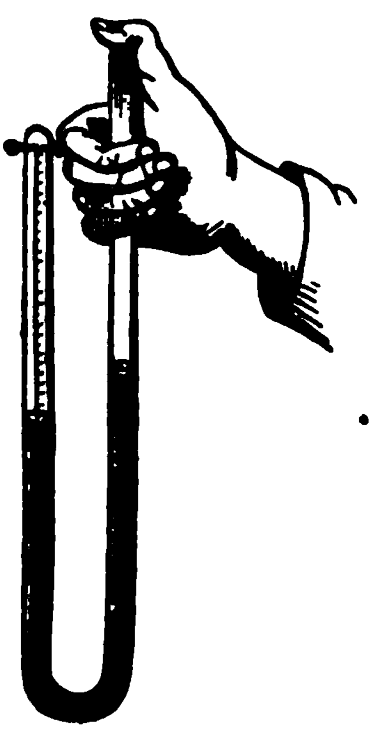
Water dissolves gases, but in very unequal quantities; some, as hydrogen, oxygen, and atmospheric air, are but little acted upon; others, as ammonia and hydrochloric acid, are absorbed to an enormous extent; and between these extremes there are various intermediate degrees. Generally, the colder the water, the more gas does it dissolve; a boiling heat disengages the whole, if the gas be not very soluble.

When water is heated in a strong vessel to a temperature above that of the ordinary boiling-point, its solvent powers are still further increased. Dr. Turner inclosed in the upper part of a high-pressure steam-boiler, worked at 300° (149°C), pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica, destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which inclosed the glass. This experiment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. Something of the sort is manifest in the Geyser springs of Iceland, which deposit siliceous sinter.[1]

Binoxide of hydrogen, sometimes called *oxygenated water*, is an exceedingly interesting substance, but unfortunately very difficult of preparation. It is formed by dissolving the binoxide of barium in dilute hydrochloric acid, carefully cooled by ice, and then precipitating the baryta by sulphuric acid; the excess of oxygen of the binoxide, instead of being disengaged as gas, unites with a portion of the water, and converts it into binoxide of hydrogen. This treatment is repeated with the same solution and fresh portions of the binoxide of barium until a considerable quantity of the latter has been consumed, and a corresponding amount of binoxide of hydrogen formed. The liquid yet contains hydrochloric acid, to get rid of which it is treated in succession with sulphate of silver and baryta-water. The whole process requires the utmost care and attention. The binoxide of barium itself is prepared by exposing pure baryta, contained in a red-hot porcelain tube, to a stream of oxygen. The solution of binoxide of hydrogen may be concentrated under the air-pump receiver until it acquires the specific gravity of 1·45. In this state it presents the aspect of a colourless, transparent, inodorous liquid, possessing remarkable bleaching powers. It is very prone to decomposition; the least elevation of temperature causes effervescence, due to the escape of oxygen gas; near 212° (100°C) it is decomposed with ex-

[1] *Phil. Mag.* Oct. 1834.

Fig. 92.



instrument is filled with mercury and inverted i vessel of the same fluid. A quantity of the air examined is then introduced, the manipulation precisely the same as with experiments over w the open end is stopped with a finger, and th transferred to the closed extremity. The instru is next held upright, and after the level of the cury has been made equal on both sides by displa a portion from the open limb by thrusting do piece of stick, the volume of air is read off. done, the open part of the tube is again filled up mercury, closed with the finger, inverted into liquid metal, and a quantity of pure hydrogen in duced, equal, as nearly as can be guessed, to a half the volume of the air. The eudiometer is more brought into an erect position, the level of mercury equalized, and the volume again read the quantity of hydrogen added is thus accura ascertained. All is now ready for the explosion; instrument is held in the way represented, the end being firmly closed by the thumb, while the knuckle of the fore-fi touches the nearer platinum wire; the spark is then passed by the aid charged jar or a good electrophorus, and explosion ensues. The air fined by the thumb in the open part of the tube acts as a spring and m rates the explosive effect. Nothing now remains but to equalize the l of the mercury by pouring a little more into the instrument, and the read off the volume for the last time.

What is required to be known from this experiment is the *diminution* mixture suffers by explosion; for since the hydrogen is in excess, and s that substance unites with oxygen in the proportion by measure of tw one, one-third part of that diminution must be due to the oxygen contai in the air introduced. As the amount of the latter is known, the propor of oxygen it contains thus admits of determination. The case supp will render this clear.

Air introduced	100 measure
Air and hydrogen	150
Volume after explosion	87
Diminution	63

$\frac{63}{3} = 21$; oxygen in the hundred measures.

The working pupil will do well to acquire dexterity in the use of this uable instrument, by practising the transference of gas or liquid from one limb to the other, &c. In the analysis of combustible gases by e sion with oxygen, solution of caustic potassa is often required to be i duced into the closed part.

Compounds of Nitrogen and Oxygen.

There are not less than five distinct compounds of nitrogen and oxy thus named and constituted: —

	Composition by weight	
	Nitrogen.	Oxygen.
:otoxide of nitrogen [1]	14	8
inoxide of nitrogen [2]	14	16
itrous acid	14	24
yponitric acid [3]	14	32
itric acid	14	40

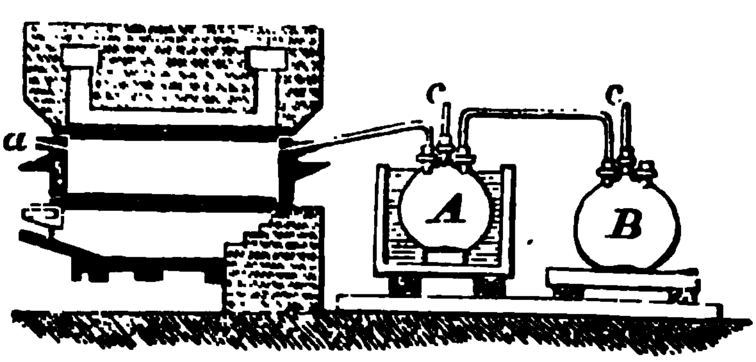
tric or Azotic Acid.—In certain parts of India, and also in other hot dry ites where rain is rare, the surface of the soil is occasionally covered saline efflorescence, like that sometimes apparent on newly-plastered ı; this substance collected, dissolved in hot water, the solution filtered made to crystallize, furnishes the highly important salt known in com- e as nitre or saltpetre; it is a compound of nitric acid and potassa. btain liquid nitric acid, equal weights of powdered nitre and oil of ɔl are introduced into a glass retort, and heat applied by means of an ınd gas-lamp or charcoal chauffer. A flask, cooled by a wet cloth, is ted to the retort, to serve for a receiver. No luting of any kind must sed.

ı the distillation advances, the red fumes which first arise disappear, but rds the end of the process again become manifest. When this happens, very little liquid passes over, while the greater part of the saline matter ıe retort is in a state of tranquil fusion, the operation may be stopped; when the retort is quite cold, water may be introduced to dissolve out bisulphate of potassa. The reaction is thus explained.

Nitre { Nitric acid → Liquid nitric acid.
Nitre { Potassa
of vitriol { Water
of vitriol { Sulphuric acid → Bisulphate of potassa.

ı the manufacture of nitric acid on the large scale, the glass retort is ıced by a cast-iron cylinder, and the receiver by a series of earthen con- ing vessels connected by tubes. (Fig. 93.) Nitrate of soda, found native eru, is often substituted for nitrate of potassa.

Fig. 93.



ɪuid nitric acid so obtained has a specific gravity of 1·5 to 1·52; it has a n yellow colour, which is due to nitrous or hyponitric acid held in solu- and which, when the acid is diluted with water, gives rise by its decom- ıon to a disengagement of nitric oxide. It is exceedingly corrosive, ng the skin deep yellow, and causing total disorganization. Poured red-hot powdered charcoal, it causes brilliant combustion; and when l to warm oil of turpentine, acts upon that substance so energetically set it on fire.

[1] Otherwise called *nitrous oxide*. [2] Otherwise called nitric oxide.
[3] Called by Professor Graham *peroxide of nitrogen*.

Pure liquid nitric acid, in its most concentrated form, is obtained by mixing the above with about an equal quantity of oil of vitriol, re-distilling collecting apart the first portion which comes over, and exposing it in a vessel slightly warmed, and sheltered from the light, to a current of dry air, made to bubble through it, which completely removes the nitrous acid. In this state the product is as colourless as water; it has the sp. gr. 1·517 at 60° (15°·5C), boils at 184° (84°·5C), and consists of 54 parts real acid, and 9 parts water. Although nitric acid in a more dilute form acts very violently upon many metals, and upon organic substances generally, this is not the case with the compound in question; even at a boiling heat it refuses to attack iron or tin, and its mode of action on lignin, starch, and similar substances, is quite peculiar, and very much less energetic than that of an acid containing more water.

A second definite compound of real nitric acid and water exists, containing 54 parts of the former to 36 parts of the latter. Its sp. gr. at 60° (15°·5C) is 1·424, and it boils at 250° (121°C). An acid weaker than this is concentrated to this point by evaporation; and one stronger, reduced to the same amount by loss of nitric acid and water in the form of the first hydrate.[1]

Absolute nitric acid, in the separate state, was unknown up to 1849, when M. Deville succeeded in obtaining this remarkable substance by exposing nitrate of silver, which is a combination of nitric acid, silver, and oxygen, to the action of chlorine gas. Chlorine and silver combine, forming chloride of silver, which remains in the apparatus, whilst oxygen and anhydrous nitric acid separate. The latter is a colourless substance, crystallizing in six-sided columns, which fuse at 86° (30°C), and boil between 118° and 122° (45° and 50°C), when they commence to be decomposed. Anhydrous nitric acid has been found to explode sometimes spontaneously. It dissolves in water with evolution of much heat, forming hydrated nitric acid. It consists of 14 parts of nitrogen and 40 parts of oxygen.

Nitric acid forms with bases a very extensive and important group of salts the nitrates, which are remarkable for all being soluble in water. The hydrated acid is of great use in the laboratory, and also in many branches of industry.

The acid prepared in the way described is apt to contain traces of chlorine from common salt in the nitre, and sometimes of sulphate from accidental splashing of the pasty mass in the retort. To discover these impurities, a portion is diluted with four or five times its bulk of distilled water and divided between two glasses. Solution of nitrate of silver is dropped into the one, and solution of nitrate of baryta into the other; if no change ensue in either case, the acid is free from the impurities mentioned.

Nitric acid has been formed in small quantity by a very curious process, namely, by passing a series of electric sparks through a portion of air, water, or an alkaline solution being present. The amount of acid so formed after many hours is very minute; still it is not impossible that powerful discharges of atmospheric electricity may sometimes occasion a trifling production of nitric acid in the air. A very minute quantity of nitric acid is also produced by the combustion of hydrogen and other substances in the atmosphere; it is also formed by the oxidation of ammonia.

Nitric acid is not so easily detected in solution in small quantities as many other acids. Owing to the solubility of all its compounds, no *precipitant* can be found for this substance. One of the best tests is its power of bleaching a solution of indigo in sulphuric acid when boiled with that liquid. The

[1] The two hydrates of nitric acid are thus expressed by symbols:—NO_5, HO and NO_5, 4HO. No compound containing two equivalents of water appears to exist.

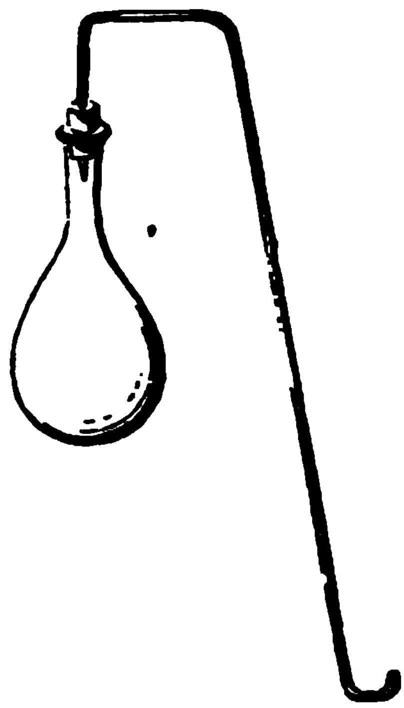
absence of chlorine must be ensured in this experiment by means which will hereafter be obvious, otherwise the result is equivocal.

Protoxide of Nitrogen; Nitrous Oxide; (laughing gas.)—When solid nitrate of ammonia is heated in a retort or flask,[1] fig. 94, furnished with a perforated cork and bent tube, it is resolved into water and nitrous oxide. The nature of the decomposition will be understood from the subjoined diagram.

Nitrate of Ammonia 80	Nitric acid 54	Nitrogen 14, Oxygen 8	Protox. nitrogen 22
		Oxygen 8, Oxygen 24	
	Ammonia 17	Nitrogen 14	Protox. nitrogen 22
		Hydrogen 3	Water 27
	Water 9		Water 9.

No particular precaution is required in the operation, save due regulation of the heat, and the avoidance of tumultuous disengagement of the gas.

Fig. 94.



Protoxide of nitrogen is a colourless, transparent, and almost inodorous gas, of distinctly sweet taste. Its specific gravity is 1·525; 100 cubic inches weigh 47·29 grains. It supports the combustion of a taper or piece of phosphorus with almost as much energy as pure oxygen; it is easily distinguished, however, from that gas by its solubility in cold water, which dissolves nearly its own volume; hence it is necessary to use tepid water in the pneumatic trough or gas-holder, otherwise great loss of gas will ensue. Nitrous oxide has been liquefied, but with difficulty; it requires, at 45° (7°·2C) a pressure of 50 atmospheres; the liquid when exposed under the bell-glass of the air-pump is rapidly converted into a snow-like solid. When mixed with an equal volume of hydrogen, and fired by the electric spark in the eudiometer, it explodes with violence, and liberates its own measure of nitrogen. Every two volumes of the gas must consequently contain two volumes of nitrogen and one volume of oxygen, the whole being condensed or contracted one-third; a constitution resembling that of vapour of water.[2]

The most remarkable feature in this gas is its intoxicating power upon the animal system. It may be respired, if quite pure, or merely mixed with atmospheric air, for a short time, without danger or inconvenience. The effect is very transient, and is not followed by depression.

Binoxide of Nitrogen; Nitric Oxide. — Clippings or turnings of copper are put into the apparatus employed for preparing hydrogen,[3] together with a little water, and nitric acid added by the funnel until brisk effervescence is excited. The gas may be collected over cold water, as it is not sensibly soluble.

The reaction is a simple deoxidation of some of the nitric acid by the copper; the metal is oxidized, and the oxide so formed is dissolved by an-

[1] Florence oil-flasks, which may be purchased at a very trifling sum, constitute exceedingly useful vessels for chemical purposes, and often supersede retorts or other expensive apparatus. They are rendered still more valuable by cutting the neck smoothly round with a hot iron, softening it in the flame of a good Argand gas-lamp, and then turning over the edge so as to form a lip, or border. The neck will then bear a tight-fitting cork without risk of splitting.

[2] See page 118.

[3] See page 111.

other portion of the acid. Nitric acid is very prone to act thus upon certain metals.

The gas obtained in this manner is colourless and transparent; in contact with air or oxygen gas it produces deep red fumes, which are readily absorbed by water; this character is sufficient to distinguish it from all other gaseous bodies. A lighted taper plunged into the gas is extinguished; lighted phosphorus, however, burns in it with great brilliancy.

The specific gravity of binoxide of nitrogen is 1·039; 100 cubic inches weigh 32·22 grains. It contains equal measures of oxygen and nitrogen gases united without condensation. When this gas is passed into a solution of protoxide of iron it is absorbed in large quantity, and a deep brown or nearly black liquid produced, which seems to be a definite compound of the two substances. The compound is again decomposed by boiling.

Nitrous Acid.—Four measures of binoxide of nitrogen are mixed with one measure of oxygen, and the gases, perfectly dry, exposed to a temperature of 0° (—17°·8C). They condense to a thin mobile green liquid. Its vapour is orange-red.

Nitrous acid is decomposed by water, being converted into nitric acid and binoxide of nitrogen. For this reason it cannot be made to unite directly with metallic oxides; nitrite of potassa may, however, be prepared by fusing nitrate of potassa, when part of its oxygen is evolved; and many other salts of nitrous acid may be obtained by indirect means.

Hyponitric Acid.—It has been doubted whether the term *acid* applied to this substance be correct, since it seems to possess the power of forming salts only in a very limited degree; the expression has, notwithstanding, been long sanctioned by use. Moreover, a beautiful crystalline lead-salt of this substance has been discovered by M. Péligot. It is formed by digesting nitrate of lead with metallic lead.

It is chiefly the vapour of hyponitric acid which forms the deep red fumes always produced when binoxide of nitrogen escapes into the air.

When carefully dried nitrate of lead is exposed to heat in a retort of hard glass, it is decomposed; protoxide of lead remains behind, while the acid is resolved into a mixture of oxygen and hyponitric acid. By surrounding the receiver with a very powerful freezing mixture, the latter is condensed to the liquid form. It is then nearly colourless, but acquires a yellow, and ultimately a red tint, as the temperature rises. At 82° (27°·8C) it boils, giving off its well-known red vapour, the intensity of the colour of which is greatly augmented by elevation of temperature.

This substance, like the preceding, is decomposed by water, being resolved into binoxide of nitrogen and nitric acid. Its vapour is absorbed by strong nitric acid, which thereby acquires a yellow or red tint, passing into green, then into blue, and afterwards disappearing altogether on the addition of successive portions of water. The deep red fuming acid of commerce, called *nitrous* acid, is simply nitric acid impregnated with hyponitric gas.[1]

Nitrogen appears to combine, under favourable circumstances, with metals When iron and copper are heated to redness in an atmosphere of ammonia, they become brittle and crystalline, but without sensible alteration of weight M. Schrötter has shown that in the case of copper, at least, this effect is

[1] Much doubt yet hangs over the true nature and relations of these two acids. According to M. Péligot, the only product of the union of binoxide of nitrogen and oxygen is *hyponitric* acid, which in the total absence of water is a white solid crystalline body, fusible at 16° (—8°·9C). At common temperatures it is an orange-yellow liquid. The same product is obtained by heating perfectly dry nitrate of lead. From these experiments it would appear *that nitrous* acid in a separate state is unknown. Ann. Chim. et Phys. 3d series, ii. 58.

used by the formation and subsequent destruction of a nitride, that is, a mpound of nitrogen with copper. When ammonia is passed over protoxide f copper heated to 570° (298°·9C), water is formed, and a soft brown owder produced, which when heated farther evolves nitrogen, and leaves etallic copper. The same effect is produced by the contact of strong acids. A similar compound of chromium with nitrogen appears to exist.

CARBON.

This substance occurs in a state of purity, and crystallized, in two distinct and very dissimilar forms, namely, as diamond, and as graphite or plumbago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of this carbon remains, obstinately retaining some of the hydrogen and oxygen, and associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, &c.

The diamond is one of the most remarkable substances known; long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the island of Borneo, and more especially Brazil, furnish this beautiful substance. It is always distinctly crystallized, often quite transparent and colourless, but now and then having a shade of yellow, pink, or blue. The origin and true geological position of the diamond are unknown; it is always found embedded in gravel and transported materials, whose history cannot be traced. The crystalline form of the diamond is that of the regular octahedron or cube, or some figure geometrically connected with these; many of the octahedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure.

Fig. 95.

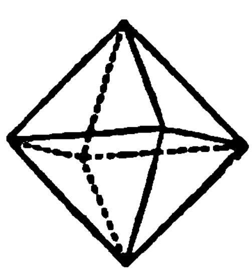


Fig. 96.

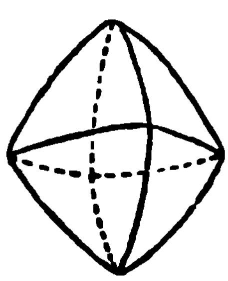


Fig. 97.

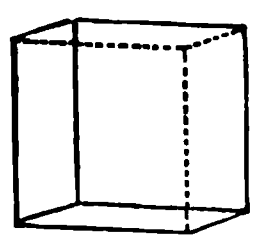
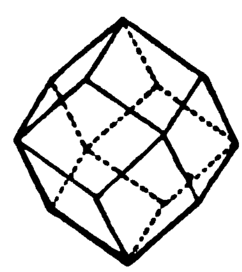


Fig. 98.



The diamond is infusible and inalterable by a very intense heat, provided air be excluded: but when heated, thus protected, between the poles of a strong galvanic battery, it is converted into coke or graphite; heated to ordinary redness in a vessel of oxygen, it burns with facility, yielding carbonic acid gas.

This is the hardest substance known; it admits of being split or cleaved without difficulty in certain particular directions, but can only be cut or abraded by a second portion of the same material; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One very curious and useful application of the diamond is made by the glazier; a *fragment* of this mineral, like a bit of flint, or any other hard substance, scratches the surface of glass; a *crystal* of diamond having the rounded octahedral figure spoken of, held in one particular position on the glass, namely, with an edge formed by the meeting of two adjacent faces presented to the surface, and then drawn along with gentle pressure, causes a deep split or cut, which penetrates to a considerable depth into the glass, and determines its fracture with perfect certainty.

Graphite, or plumbago, appears to consist essentially of pure carbon, although most specimens contain iron, the quantity of which varies from a mere trace up to five per cent. Graphite is a somewhat rare mineral; the finest, and most valuable for pencils, is brought from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate-beds of that district. Crystals are not common; when they occur, they have the figure of a short six-sided prism:—a form bearing no geometric relation to that of the diamond.

Graphite is often formed artificially in certain metallurgic operations; the brilliant scales which sometimes separate from melted cast iron on cooling, called by the workmen "kish," consist of graphite.

Lampblack, the soot produced by the imperfect combustion of oil or resin, is the best example that can be given of carbon in its uncrystallized or *amorphous* state. To the same class belong the different kinds of charcoal. That prepared from wood, either by distillation in a large iron retort, or by the smothered combustion of a pile of fagots partially covered with earth, is the most valuable as fuel. Coke, the charcoal of pit-coal, is much more impure: it contains a large quantity of earthy matter, and very often sulphur: the quality depending very much upon the mode of preparation. Charcoal from bones and animal matters in general is a very valuable substance, on account of the extraordinary power it possesses of removing colouring matters from organic solutions: it is used for this purpose by the sugar-refiners to a very great extent, and also by the manufacturing and scientific chemist.[1] The property in question is possessed by all kinds of charcoal in a small degree.

Charcoal made from box, or other dense wood, has a property of condensing into its pores gases and vapours; of ammoniacal gas it is said to absorb not less than ninety times its volume, while of hydrogen it takes up less than twice its own bulk, the quantity being apparently connected with the property in the gas of suffering liquefaction. This effect, as well as that of the decolorizing power, no doubt depends in some way upon the same peculiar action of surface so remarkable in the case of platinum in a mixture of oxygen and hydrogen.[2]

Compounds of Carbon and Oxygen.

There are two direct inorganic compounds of carbon and oxygen, called carbonic oxide and carbonic acid; their composition may be thus stated:—

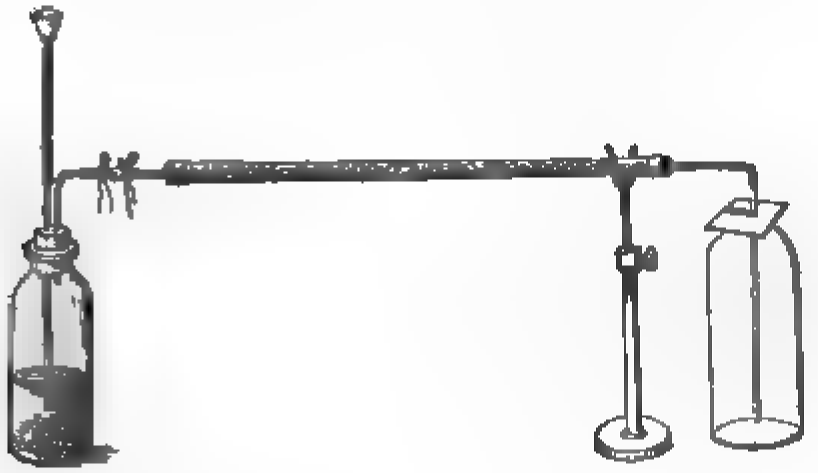
	Composition by weight.	
	Carbon.	Oxygen.
Carbonic oxide	6	8
Carbonic acid	6	16

[1] It removes from solution in water the vegetable bases, bitter principles and astringent substances, when employed in excess, requiring from twice to twenty times their weight for total precipitation. A solution of iodine in water, or iodide of potassium, is quickly deprived of colour. Metallic salts dissolved in water or diluted alcohol are precipitated, though not entirely, requiring about thirty times their weight of animal charcoal. Arsenious acid is totally carried out of solution. In these cases it acts in three different ways: the salt is absorbed unaltered: the oxide in the salt may be reduced: or, the salts precipitated in a basic condition, the solution showing an acid reaction as soon as the carbon begins to act. It is in this last case especially that traces of the bases can be detected, the acid set free preventing their total precipitation. The precipitation may hence be prevented by adding an excess of acid, and the bases after precipitation may be dissolved out by boiling with an acid solution.—Warrington, Mem. Chim. Soc. 1845; Garrod, Pharm. Journ. 1845; Weppen, Ann. de Chim. 1845.—R. B.

[2] Carbon is a combustible uniting with oxygen and producing carbonic acid. Its different forms exhibit much difference in this respect: in the very porous condition of charcoal it burns readily, while in its most dense form, the diamond, it requires a bright red heat and pure oxygen. In the form of charcoal it conducts heat slowly and electricity readily. Carbon is insoluble in water and not liable to be affected by air and moisture. It retards putrefaction.—*R. B.*

bonic Acid is always produced when charcoal burns in air or in oxygen
it is most conveniently obtained, however, for study, by decomposing
bonate with one of the stronger acids. For this purpose, the apparatus
nerating hydrogen may be again employed; fragments of marble are
nto the bottle, with enough water to cover the extremity of the funnel-
and hydrochloric or nitric acid added by the latter, until the gas is
y disengaged. Chalk-powder and dilute sulphuric acid may be used
ad. The gas may be collected over water, although with some loss; or

Fig. 99.

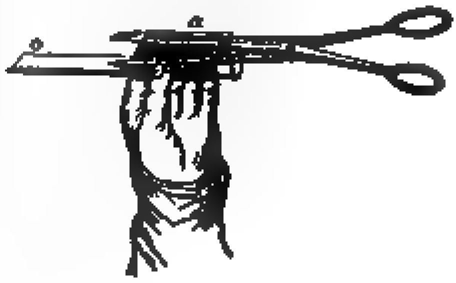


conveniently, by displacement, if it be required dry, as shown in fig.
The long drying-tube is filled with fragments of chloride of calcium,
the heavy gas is conducted to the bottom of the vessel in which it is to
ceived, the mouth of the latter being lightly closed.[1]
arbonic acid gas is colourless; it has an agreeable pungent taste and
r, but cannot be respired for a moment without insensibility following.
pecific gravity is 1·524,[2] 100 cubic inches weighing 47·26 grains.
his gas is very hurtful to animal life, even when largely diluted with air;
ts as a narcotic poison. Hence the danger arising from imperfect ven-
on, the use of fire-places and stoves of all kinds unprovided with proper
neys, and the crowding together of many individuals in houses and
without efficient means for renewing the air; for carbonic acid is con-
ly disengaged during the process of respiration, which, as we have seen,
108,) is nothing but a process of slow combustion. This gas is some-
emitted in large quantity from the earth in volcanic districts, and it is
antly generated where organic matter is in the act of undergoing fer-
ive decomposition. The fatal "after-damp" of the coal-mines contains
ge proportion of carbonic acid.

---

connecting tube-apparatus for conveying gases or cold liquids, not corrosive, little
of caoutchouc about an inch long, are in-
ibly useful. These are made by bending
of sheet India-rubber, *a*, fig. 100, loosely
a glass tube or rod, *o*, and cutting off the
luous portion with sharp scissors. The
nt edges of the caoutchouc, pressed strongly
er, cohere completely, provided they have
en soiled by touching with the fingers, and
be is perfect. The connectors are secured
o or three turns of thin silk cord. The
tubes are sold by weight, and are easily
n the flame of a spirit-lamp, and, when
ary, cut by scratching with a file, and
ng asunder.

Fig. 100.



[2] *Dulong and Berzelius.*

A lighted taper plunged into carbonic acid is instantly extinguished, even to the red-hot snuff. When diluted with three times its volume of air, it still has the power of extinguishing a light. The gas is easily known from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali or by lime-water; the turbidity communicated to the latter from the production of insoluble carbonate of lime is very characteristic.

Cold water dissolves about its own volume of carbonic acid, whatever be the density of the gas with which it is in contact; the solution temporarily reddens litmus paper. In common soda-water, and also in effervescent wines, examples may be seen of this solubility of the gas. Even boiling water absorbs a perceptible quantity.

Some of the interesting phenomena attending the liquefaction of carbonic acid have been already described; it requires for the purpose a pressure of between 27 and 28 atmospheres at 32° (0°C), according to Mr. Addams. The liquefied acid is colourless and limpid, lighter than water, and four times more expansible than air; it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and bisulphide of carbon, and is insoluble in water and fat oils. It is probably destitute when in this condition of all properties of an acid.[1]

Carbonic acid exists, as already mentioned, in the air; relatively, its quantity is but small, but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose for which it is designed, namely, to supply to plants their carbon, these latter having the power, by the aid of their green leaves, of decomposing carbonic acid, retaining the carbon, and expelling the oxygen. The presence of light is essential to this extraordinary effect, but of the manner of its execution we are yet ignorant.

The carbonates form a very large and important group of salts, some of which occur in nature in great quantities, as the carbonates of lime and magnesia.

Carbonic Oxide. — When carbonic acid is passed over red-hot charcoal or metallic iron, one-half of its oxygen is removed, and it becomes converted into carbonic oxide. A very good method of preparing this gas is to introduce into a flask fitted with a bent tube some crystallized oxalic acid, or salt of sorrel, and pour upon it five or six times as much strong oil of vitriol. On heating the mixture the organic acid is resolved into water, carbonic acid, and carbonic oxide; by passing the gases through a strong solution of caustic potassa, the first is withdrawn by absorption, while the second remains unchanged. Another, and it may be preferable method, is to heat finely-powdered yellow ferrocyanide of potassium with eight or ten times its weight of concentrated sulphuric acid. The salt is entirely decomposed, yielding a most copious supply of perfectly pure carbonic oxide gas, which may be collected over water in the usual manner.[2]

Carbonic oxide is a combustible gas; it burns with a beautiful pale blue flame, generating carbonic acid. It has never been liquefied. It is colourless, has very little odour, and is extremely poisonous, even worse than carbonic acid. Mixed with oxygen, it explodes by the electric spark, but

[1] When relieved of pressure it immediately boils, and seven parts out of eight assume the gaseous state, the rest becoming solid at —90° (67°·7C) (Mitchell). Solid carbonic acid mixed with ether produces in vacuo a very intense cold (—165° [109°·4C] Faraday), capable of solidifying many gases when aided by pressure. Liquid carbonic acid immersed in this mixture becomes a solid so clear and transparent that its condition cannot be detected until a portion again becomes liquid. — R. B.

[2] See a paper by the author, in Memoirs of Chem. Soc. of London, i. 251. 1 eq. crystallized ferrocyanide of potassium. and 6 eq. oil of vitriol, yield 6 eq. carbonic oxide, 2 eq. sulphate of potassa, 3 eq. sulphate of ammonia, and 1 eq. protosulphate of iron.

ith some difficulty. Its specific gravity is 0·978; 100 cubic inches weigh)·21 grains.

The relation by volume of these oxides of carbon may thus be made intelligible:—carbonic acid contains its own volume of oxygen, that gas suffer-g no change of bulk by its conversion. One measure of carbonic oxide ixed with half a measure of oxygen and exploded, yields one measure of arbonic acid; hence carbonic oxide contains half its volume of oxygen.

Carbonic oxide unites with chlorine under the influence of light, forming pungent, suffocating compound, possessing acid properties, called phosgene as, or chloro-carbonic acid. It is made by mixing equal volumes of caronic oxide and chlorine, both perfectly dry, and exposing the mixture to unshine; the gases unite quietly, the colour disappears, and the volume ecomes reduced to one-half. It is decomposed by water.

SULPHUR.

This is an elementary body of great importance and interest. Sulphur often found in a free state in connection with deposits of gypsum and rockalt; its occurrence in volcanic districts is probably accidental. Sicily furishes a large proportion of the sulphur employed in Europe. In a state of ombination with iron and other metals, and as sulphuric acid, united to me and magnesia, it is also abundant.

Pure sulphur is a pale yellow brittle solid, of well-known appearance. It elts when heated, and distils over unaltered, if air be excluded. The crysals of sulphur exhibit two distinct and incompatible forms, namely, an ocahedron with rhombic base (fig. 101), which is the figure of native sulphur, nd that assumed when sulphur separates from solution at common temperatures, as when a solution of sulphur in bisulphide of carbon is exposed to low evaporation in the air; and a lengthened prism (fig. 103), having no elation to the preceding; this happens when a mass of sulphur is melted, nd, after partial cooling, the crust at the surface broken, and the fluid portion poured out. Fig. 102 shows the result of such an experiment.

Fig. 101.

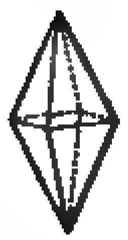


Fig. 102.

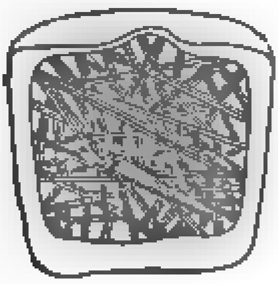
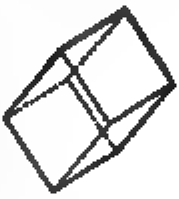


Fig. 103.



The specific gravity of sulphur varies according to the form in which it is rystallized. The octahedral variety has a specific gravity 2·045; the prisatic variety a specific gravity 1·982.

Sulphur melts at 232° (111°·1C); at this temperature it is of the colour f amber, and thin and fluid as water; when farther heated, it begins to nicken, and to acquire a deeper colour; and between 430° (221°C) and 480° 249°C), it is so tenacious that the vessel in which it is contained may be verted for a moment without the loss of its contents. If in this state it be oured into water, it retains for many hours its remarkable soft and flexible ondition, which should be looked upon as the amorphous state of sulphur. fter a while it again becomes brittle and crystalline. From the temperare last mentioned to the boiling-point, about 792° (400°C), sulphur again

Hyponitric acid 46	Nitrogen	14	Binoxide of nitrogen 30
	Oxygen	16	
	Oxygen	16	
Sulphurous acid 64	Sulphur	32	
	Oxygen	32	
Water		18	Hydrated sulphuric acid 98

Such is the simplest view that can be taken of the production of sulphuric acid in the leaden chamber, but it is too much to affirm that it is strictly true; it may be more complex. When a little water is put at the bottom of a large glass globe, so as to maintain a certain degree of humidity in the air within, and sulphurous and hyponitric acids are introduced by separate tubes, symptoms of chem cal action become immediately evident, and after a little time a white crystalline matter is observed to condense on the sides of the vessel. This substance appears to be a compound of sulphuric acid, nitrous acid, and a little water.[1] When thrown into water, it is resolved into sulphuric acid, binoxide of nitrogen, and nitric acid. This curious body is certainly very often produced in large quantity in the leaden chambers; but that its production is indispensable to the success of the process, and constant when the operation goes on well, and the hyponitric acid is not in excess, may perhaps admit of doubt.

The water at the bottom of the chamber thus becomes loaded with sulphuric acid; when a certain degree of strength has been reached, it is drawn off and concentrated by evaporation, first in leaden pans, and afterwards in stills of platinum, until it attains a density (when cold) of 1·84, or thereabouts; it is then transferred to carboys, or large glass bottles fitted in baskets, for sale. In Great Britain this manufacture is one of great national importance, and is carried on to a vast extent. An inferior kind of acid is sometimes made by burning iron pyrites, or poor copper ore, as a substitute for Sicilian sulphur; this is chiefly used by the makers for their own consumption; it very frequently contains arsenic.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40 parts real acid, and 9 parts water. It is a colourless, oily liquid, having a specific gravity of about 1·85, of intensely acid taste and reaction. Organic matter is rapidly charred and destroyed by this substance. At the temperature of —15° (—26°·1C) it freezes; at 620° (326°·6C) it boils, and may be distilled without decomposition. Oil of vitriol has a most energetic attraction for water; it withdraws aqueous vapours from the air, and when diluted, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric acid; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystalline substance separates, which is a hydrate containing half as much water as the common liquid acid. Then, again, a mixture of 49 parts strong liquid acid and 9 parts water, congeals or crystallizes at a temperature above

[1] M. Gaultier de Claubry assigned to this curious substance the composition expressed by the formula $4HO, 2NO_3+5SO_3$, and this view has generally been received by recent chemical writers. M. de la Provostaye has since shown that a compound, possessing all the essential properties of the body in question, may be formed by bringing together, in a sealed glass tube, liquid sulphurous acid and liquid hyponitric acid, both free from water. The white crystalline solid soon begins to form, and at the expiration of twenty-six hours the reaction appears complete. The new product is accompanied by an exceedingly volatile greenish liquid having the characters of nitrous acid. The white substance, on analysis, was found to contain the elements of two equivalents of sulphuric acid and one of nitrous acid, or NO_3+2SO_3. M. de la Provostaye very ingeniously explains the anomalies in the different analyses of the leaden chamber product, by showing that the pure substance forms crystallizable combinations with different proportions of liquid sulphuric acid. (Ann. Chim. et Phys. lxxiii. 362.)

(0°C), and remains solid even at 45° (7°·2C). Lastly, when a very ıte acid is concentrated by evaporation *in vacuo* over a surface of oil of ·iol, the evaporation stops when the real acid and water bear to each er the proportion of 40 to 27.

When good Nordhausen oil of vitriol is exposed in a retort to a gentle ıt, and a receiver cooled by a freezing mixture fitted to it, a volatile ostance distils over in great abundance, which condenses into beautiful, ite, silky crystals, resembling those of asbestus; this bears the name of hydrous sulphuric acid. When put into water it hisses like a hot iron, m the violence with which combination occurs; exposed to the air even r a few moments, it liquefies by absorption of moisture, forming common uid sulphuric acid. It forms an exceedingly curious compound with dry ımoniacal gas, quite distinct from ordinary sulphate of ammonia, and ich indeed possesses none of the characters of a sulphate. This interest- g substance may also be obtained by distilling the most concentrated oil vitriol with a sufficient quantity of anhydrous phosphoric acid.

Sulphuric acid, in all soluble states of combination, may be detected with e greatest ease by solution of nitrate of baryta, or chloride of barium. A ite precipitate is produced, which does not dissolve in nitric acid.

Hyposulphurous Acid.—By digesting sulphur with a solution of sulphite potassa or soda, a portion of that substance is dissolved, and the liquid, ' slow evaporation, furnishes crystals of the new salt. The acid cannot be lated; when hydrochloric acid is added to a solution of a hyposulphite, e acid of the latter is almost instantly resolved into sulphur, which pre- pitates, and into sulphurous acid, easily recognized by its odour. The ost remarkable feature of the alkaline hyposulphites is their property of solving certain insoluble salts of silver, as the chloride—a property which s lately conferred upon them a considerable share of importance in rela- n to the art of photogenic drawing.

Hyposulphuric Acid, Dithionic Acid.—This is prepared by suspending ely divided binoxide of manganese in water artificially cooled, and then nsmitting a stream of sulphurous acid gas; the binoxide becomes pro- ide, half its oxygen converting the sulphurous acid into hyposulphuric. e hyposulphate of manganese thus prepared is decomposed by a solution pure hydrate of baryta, and the barytic salt, in turn, by enough sul- uric acid to precipitate the base. The solution of hyposulphuric acid y be concentrated by evaporation *in vacuo*, until it acquires a density of 47: pushed farther, it decomposes into sulphuric and sulphurous acids. as no odour, is very sour, and forms soluble salts with baryta, lime, and toxide of lead.

Sulphuretted hyposulphuric Acid, Trithionic Acid.—A substance accidentally ned by M. Langlois,[1] in the preparation of hyposulphite of potassa, by tly heating with sulphur a solution of carbonate of potassa, saturated h sulphurous acid. The salts bear a great resemblance to those of hypo- phurous acid, but differ completely in composition, while the acid itself ot quite so prone to change. It is obtained by decomposing the potassa by hydrofluosilicic acid; it may be concentrated under the receiver of air-pump, but it is gradually decomposed into sulphur, sulphurous and phuric acids.

Bisulphuretted hyposulphuric Acid, Tetrathionic Acid.—This was discovered MM. Fordos and Gélis.[2] When iodine is added to a solution of hyposul- te of soda, a large quantity of that substance is dissolved, and a clear, urless solution obtained, which, besides iodide of sodium, contains a salt

[1] *Ann. Chim. et Phys.* 3d series, iv. 77.
[2] *Ib.* 3d series, vi. 484

of a peculiar acid, richer in sulphur than the preceding. By suitable means, the new substance can be eliminated, and obtained in a state of solution. It very closely resembles hyposulphuric acid. The same acid is produced by the action of sulphurous acid on subchloride of sulphur.

Trisulphuretted hyposulphuric Acid, Pentathionic Acid.—Another acid of sulphur has been announced by M. Wackenroder, who formed it by the action of sulphuretted hydrogen on sulphurous acid. It is described as colourless and inodorous, of acid and bitter taste, and capable of being concentrated to a considerable extent by cautious evaporation. It contains S_5O_5; under the influence of heat, it is decomposed into sulphur, sulphurous and sulphuric acid and sulphuretted hydrogen. The salts of pentathionic acids are nearly all soluble. The baryta salt crystallizes from alcohol in square prisms. The acid is also formed when hyposulphate of lead is decomposed by sulphuretted hydrogen, and when protochloride of sulphur is heated with sulphurous acid.

Sulphurous acid unites, under peculiar circumstances, with chlorine, and also with iodine, forming compounds, which have been called chloro- and iodo-sulphuric acids. They are decomposed by water. It also combines with dry ammoniacal gas, giving rise to a remarkable compound; and with nitric oxide also, in presence of an alkali.

SELENIUM.

This is a very rare substance, much resembling sulphur in its chemical relations, and found in association with that element in some few localities, or replacing it in certain metallic combinations, as in the selenide of lead of Clausthal, in the Hartz.

Selenium is a reddish-brown solid body, somewhat translucent, and having an imperfect metallic lustre. Its specific gravity, when rapidly cooled after fusion, is 4·3. At 212° (100°C), or a little above, it melts, and at 650° (343°·8C) boils. It is insoluble in water, and exhales, when heated in the air, a peculiar and disagreeable odour, which has been compared to that of decaying horseradish. There are three oxides of selenium, two of which correspond respectively to sulphurous and sulphuric acids, while the third has no known analogue in the sulphur series.

	Composition by weight.	
	Selenium.	Oxygen.
Oxide of selenium	39·5	8
Selenious acid	39·5	16
Selenic acid	39·5	24

Oxide.—Formed by heating selenium in the air. It is a colourless gas, slightly soluble in water, and has the remarkable odour above described. It has no acid properties.

Selenious Acid.—This is obtained by dissolving selenium in nitric acid, and evaporating to dryness. It is a white, soluble, deliquescent substance, of distinct acid properties, and may be sublimed without decomposition. Sulphurous acid decomposes it, precipitating the selenium.

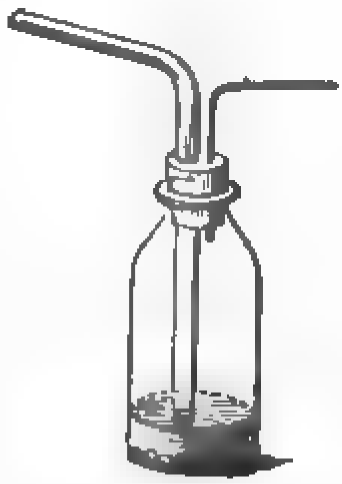
Selenic Acid.—Prepared by fusing nitrate of potassa or soda with selenium, precipitating the seleniate so produced by a salt of lead, and then decomposing the compound by sulphuretted hydrogen. The hydrated acid strongly resembles oil of vitriol; but, when very much concentrated, decomposes, by the application of heat, into selenious acid and oxygen. The seleniates bear the closest analogy to the sulphates in every particular.

PHOSPHORUS.

Phosphorus in a state of phosphoric acid is contained in the ancient unstratified rocks, and in the lavas of modern origin. As these disintegrate and crumble down into fertile soil, the phosphates pass into the organism of plants, and ultimately into the bodies of the animals to which these latter serve for food. The earthy phosphates play a very important part in the structure of the animal frame, by communicating stiffness and inflexibility to the bony skeleton.

This element was discovered in 1669 by Brandt, of Hamburg, who prepared it from urine. The following is an outline of the process now adopted. Thoroughly calcined bones are reduced to powder, and mixed with two-thirds of their weight of sulphuric acid, diluted with a considerable quantity of water; this mixture, after standing some hours, is filtered, and the nearly insoluble sulphate of lime washed. The liquid is then evaporated to a syrupy consistence, mixed with charcoal powder, and the desiccation completed in an iron vessel exposed to a high temperature. When quite dry, it is transferred to a stoneware retort, to which a wide bent tube is luted, dipping a little way into the water contained in the receiver. A narrow tube serves to give issue to the gases, which are conveyed to a chimney. (Fig. 104.) This manufacture is now conducted on a very great scale, the consumption of phosphorus, for the apparently trifling article of instantaneous light matches, being something prodigious.

Fig. 104.



Phosphorus, when pure, very much resembles in appearance imperfectly bleached wax, and is soft and flexible at common temperatures. Its density is 1·77, and that of its vapour 4·35, air being unity. At 108° (42°·2C) it melts, and at 550° (287°·7C) boils. It is insoluble in water, and is usually kept immersed in that liquid, but dissolves in oils, in native naphtha, and especially in bisulphide of carbon. When set on fire in the air, it burns with a bright flame, generating phosphoric acid. Phosphorus is exceedingly inflammable; it sometimes takes fire by the heat of the hand, and demands great care in its management; a blow or hard rub will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, which in the dark is luminous. This effect is chiefly due to a slow combustion which the phosphorus undergoes by the oxygen of the air, and upon it depends one of the methods employed for the analysis of the atmosphere, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapour of ether, or some essential oil; it may even be distilled in an atmosphere containing vapour of oil of turpentine in considerable quantity. Neither does the action go on in pure oxygen, at least at the temperature of 60° (15°·5C), which is very remarkable; but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbonic acid, oxidation is set up. According to the researches of Marchand, evaporation of phosphorus causes a luminosity, even when there is no oxidation.

A very remarkable modification of this element is known by the name of amorphous phosphorus. It was discovered by Schrötter, and may be made by exposing for fifty hours common phosphorus to a temperature of about 464° to 482° *(240° to 250°C)* in an atmosphere which is unable to act chemi-

cally upon it. At this temperature it becomes red and opaque, and insoluble in bisulphide of carbon, whereby it may be separated from ordinary phosphorus. It may be obtained in compact masses when common phosphorus is kept for eight days at a constant high temperature. It is a coherent, reddish-brown, infusible substance, of specific gravity between 2·089 and 2·106. It does not become luminous in the dark until its temperature is raised to about 392° (200°C), nor has it any tendency to combine with the oxygen of the air. When heated to 500° (260°C), it is reconverted into ordinary phosphorus.

Compounds of Phosphorus and Oxygen.—These are four in number, and have the composition indicated below.

	Composition by weight	
	Phosphorus.	Oxygen.
Oxide of phosphorus	64	8
Hypophosphorous acid	32	8
Phosphorous acid	32	24
Phosphoric acid [1]	32	40

Oxide of Phosphorus.—When phosphorus is melted beneath the surface of hot water, and a stream of oxygen gas forced upon it from a bladder, combustion ensues, and the phosphorus is converted in great part into a brick-red powder, which is the substance in question. It is decomposed by heat into phosphorus and phosphoric acid.

Hypophosphorous Acid.—When phosphide of barium is put into hot water, that liquid is decomposed, giving rise to phosphoretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta; the first escapes as gas, and the two acids remain in union with the baryta. By filtration the soluble hypophosphite is separated from the insoluble phosphate. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the base, the hypophosphorous acid is obtained in solution. By evaporation it may be reduced to a syrupy consistence.

The acid is very prone to absorb more oxygen, and is therefore a powerful deoxidizing agent. All its salts are soluble in water.

Phosphorous Acid.—Phosphorous acid is formed by the slow combustion of phosphorus in the atmosphere; or by burning that substance by means of a very limited supply of air, in which case it is anhydrous, and presents the aspect of a white powder. The hydrated acid is more conveniently prepared by adding water to the terchloride of phosphorus, when mutual decomposition takes place, the oxygen of the water being transferred to the phosphorus, generating phosphorous acid, and its hydrogen to the chlorine, giving rise to hydrochloric acid. By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue on cooling crystallizes.

Hydrated phosphorous acid is very deliquescent and very prone to attract oxygen and pass into phosphoric acid. When heated in a close vessel, it is resolved into hydrated phosphoric acid and pure phosphoretted hydrogen gas. It is composed of 56 parts real acid and 27 parts water. [2]

The phosphites are of little importance.

Phosphoric Acid.—When phosphorus is burned under a bell-jar by the aid of a copious supply of dry air, snow-like anhydrous phosphoric acid is pro-

[1] In symbols—Oxide of phosphorus .... P_2O
Hypophosphorous acid .... PO
Phosphorous acid .... PO_3
Phosphoric acid .... PO_5
Equivalent of phosphorus, 32

[2] *Or*, $3HO, PO^3$.

ent quantity. This substance exhibits as much attraction for ydrous sulphuric acid; exposed to the air for a few moments, s to a liquid, and when thrown into water, combines with the xplosive violence. Once in the state of hydrate, the water be separated.

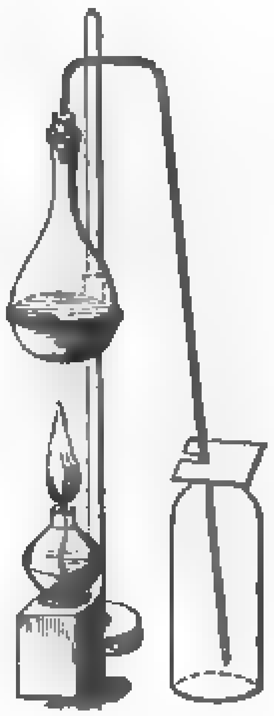
ic acid of moderate strength is heated in a retort to which a onnected, and fragments of phosphorus added singly, taking the violence of the action to subside between each addition, rus is oxidized to its maximum, and converted into phosphoric stilling off the greater part of the acid, transferring the residue to a platinum vessel, and then cautiously raising the heat to hydrated acid may be obtained pure. This is the *glacial phos-*f the Pharmacopœia.

thod consists in taking the acid phosphate of lime produced by f sulphuric acid on bone-earth, precipitating it with a slight bonate of ammonia, separating by a filter the insoluble lime-n evaporating and igniting in a platinum vessel the mixed d sulphate of ammonia. Hydrated phosphoric acid alone remains acid thus obtained is not remarkable for its purity. One of antageous methods of preparing phosphoric acid on the large ate of purity, is to burn phosphorus in a stream of dry atmo-y the aid of a proper apparatus, not difficult to contrive, in ocess may be carried on continuously. The anhydrous acid be preserved in that state, or converted into hydrate or glacial addition of water and subsequent fusion in a platinum vessel. of phosphoric acid is exceedingly deliquescent, and requires to closely stopped bottle. It contains 72 parts real acid, and 9

acid is a powerful acid; its solution has an intensely sour ldens litmus paper; it is not poisonous.

few bodies that present a greater degree of interest to the this substance; the extraordinary changes is undergo by the action of heat, chiefly to us by the admirable researches of s, will be found described in connection ral history of saline compounds.

Fig. 105.



CHLORINE.

ance is a member of a small natural group esides iodine, bromine and fluorine. So ee of resemblance exists between these their chemical relations, that the history lmost serve, with a few little alterations, e rest.

s a very abundant substance; in common in combination with sodium. It is most ed by pouring strong liquid hydrochloric ely-powdered black oxide of manganese, a retort or flask, and applying a gentle y yellow gas is disengaged, which is the question. (Fig 105.)

collected over warm water, or by displace-ercurial trough cannot be employed, as rapidly acts upon the metal, and becomes

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n χλωρός, *yellowish-green*, the name given to it by Sir H. Davy.

The reaction is very easily explained. Hydrochloric acid is a compound of chlorine and hydrogen; when this is mixed with a metallic protoxide, double interchange of elements takes place, water and chloride of the metal being produced. But when some of the *binoxides* are substituted, an additional effect ensues, namely, the decomposition of a second portion of hydrochloric acid by the oxygen in excess, the hydrogen of which is withdrawn, and the chlorine set free.

Hydrochloric acid	Chlorine	Chlorine.
	Hydrogen	Water.
Binoxide of manganese	Oxygen	
	Manganese	Chloride of manganese.
	Oxygen	
Hydrochloric acid	Chlorine	
	Hydrogen	Water.

Chlorine was discovered in 1774, by Scheele, but its nature was long misunderstood. It is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled even in exceedingly small quantity. It is soluble to a considerable extent in water, that liquid absorbing at 60° (15°·5C) about twice its volume, and acquiring the colour and odour of the gas. When this solution is exposed to light, it is slowly changed by decomposition of water into hydrochloric acid, the oxygen being at the same time liberated. When moist chlorine gas is exposed to a cold of 32° (0°C), yellow crystals are formed which consist of a definite compound of chlorine and water containing 35·5 parts of the former to 90 of the latter.

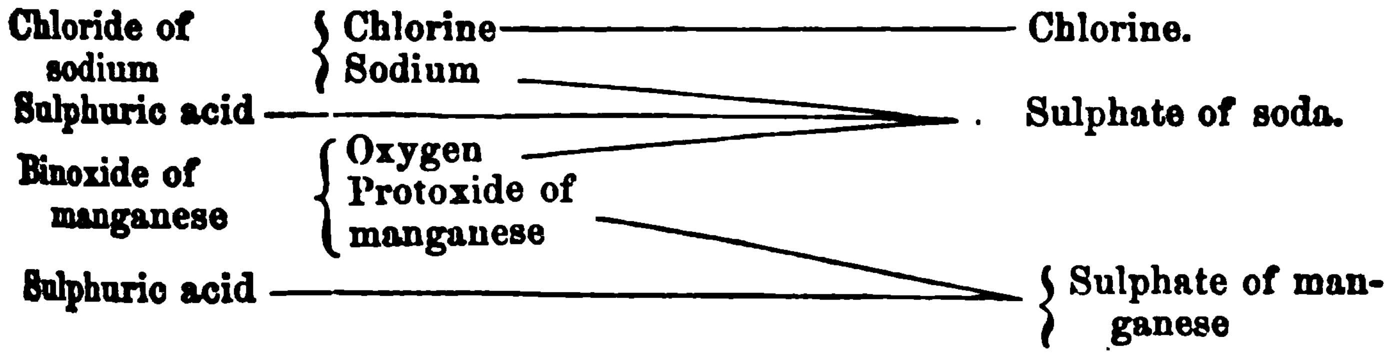
Chlorine has a specific gravity of 2·47, 100 cubic inches weighing 76·6 grains. Exposed to a pressure of about four atmospheres, it condenses to a yellow limpid liquid.

This substance has but little attraction for oxygen, its chemical energies being principally exerted towards hydrogen and the metals. When a lighted taper is plunged into the gas, it continues to burn with a dull red light, and emits a large quantity of smoke, the hydrogen of the wax being alone consumed, and the carbon separated. If a piece of paper be wetted with oil of turpentine, and thrust into a bottle filled with chlorine, the chemical action of the latter upon the hydrogen is so violent as to cause inflammation, accompanied by a copious deposit of soot. Although chlorine can, by indirect means, be made to combine with carbon, yet this never occurs under the circumstances described.

Phosphorus takes fire spontaneously in chlorine; it burns with a pale and feebly luminous flame. Several of the metals, as copper-leaf, powdered antimony, and arsenic, undergo combustion in the same manner. A mixture of equal measures chlorine and hydrogen explodes with violence on the passage of an electric spark, or on the application of a lighted taper, hydrochloric acid gas being formed. Such a mixture may be retained in the dark for any length of time without change; exposed to diffuse daylight, the two gases slowly unite, while the direct rays of the sun induce instantaneous explosion.

The most characteristic property of chlorine is its bleaching power; the most stable organic colouring principles are instantly decomposed and destroyed by this remarkable agent: indigo, for example, which resists the action of strong oil of vitriol, is converted by chlorine into a brownish substance, to which the blue colour cannot be restored. The presence of water is essential to these changes, for the gas in a state of perfect dryness is incapable even of affecting litmus.

Chlorine is largely used in the arts for bleaching linen and cotton goods, rags for the manufacture of paper, &c. For these purposes, it is sometimes employed in the state of gas, sometimes in that of solution in water, but more frequently in combination with lime, forming the substance called bleaching-powder. When required in large quantities, it is often made by pouring slightly diluted oil of vitriol upon a mixture of common salt and oxide of manganese contained in a large leaden vessel. The decomposition which ensues may be thus represented:—

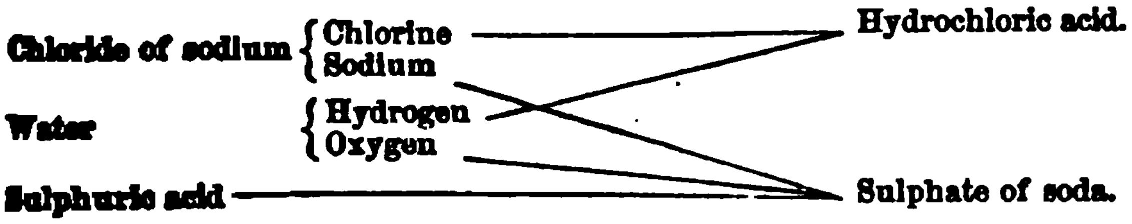


Chlorine is one of the best and most potent substances that can be used for the purpose of disinfection, but its employment requires care. Bleaching-powder mixed with water, and exposed to the air in shallow vessels, becomes slowly decomposed by the carbonic acid of the atmosphere, and the chlorine evolved; if a more rapid disengagement be wished, a little acid of any kind may be added. In the absence of bleaching-powder, either of the methods for the production of the gas described may be had recourse to, always taking care to avoid an excess.

Chloride of Hydrogen; Hydrochloric, Chlorhydric or Muriatic Acid.—This substance in a state of solution in water, has been long known. The gas is prepared with the utmost ease by heating in a flask, fitted with a cork and bent tube, a mixture of common salt and oil of vitriol, diluted with a small quantity of water; it must be collected by displacement, or over mercury. It is a colourless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odour, but is infinitely less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrochloric acid gas has a density 1·269. It is exceedingly soluble in water, that liquid taking up at the temperature of the air about 418 times its bulk. The gas and solution are powerfully acid.

The action of oil of vitriol on common salt, or any analogous substance, is thus easily explained: —



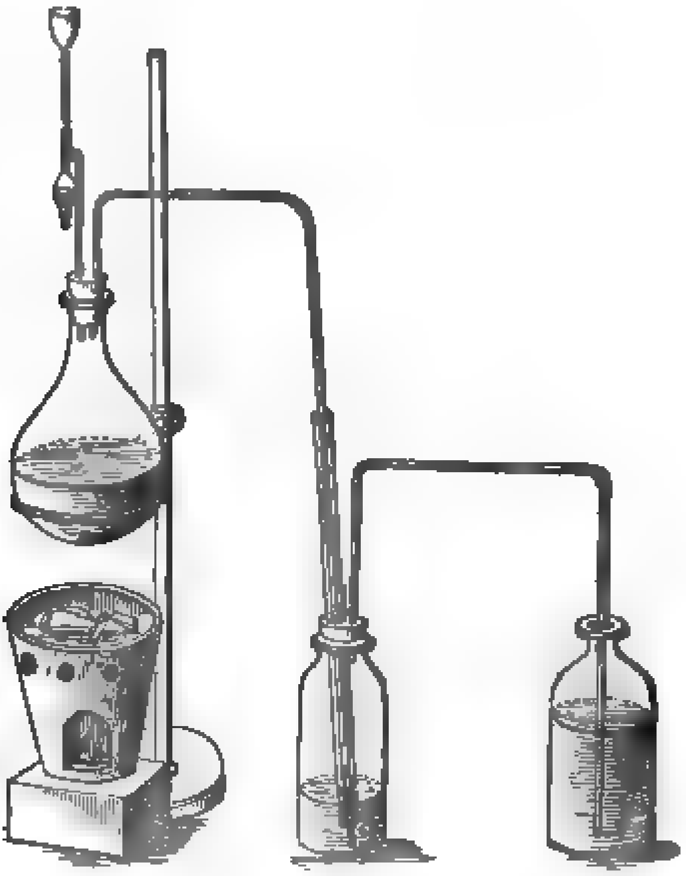
The composition of this substance may be determined by synthesis: when a measure of chlorine and a measure of hydrogen are fired by the electric spark, two measures of hydrochloric acid gas result, the combination being unattended by change of volume. By weight it contains 35·5 parts chlorine and 1 part hydrogen.

Solution of hydrochloric acid, the liquid acid of commerce, is a very important preparation, and of extensive use in chemical pursuits; it is best prepared by the following arrangement:

A large glass flask, containing a quantity of common salt, is fitted with a

cork and bent tube, in the manner represented in fig. 106; the latter p
through and below a second short tube into a wide-necked bottle, cont

Fig. 106



a little water, into which the open tube dips. A bent tube is adapted
other hole in the cork of the wash-bottle, so as to convey the purif
into a quantity of distilled water, by which it is instantly absorbed
joints are made air-tight by melting over the corks a little yellow wa:

Oil of vitriol, about equal in weight to the salt, is then slowly intr
by the funnel; the disengaged gas is at first wholly absorbed by the
in the wash-bottle, but when this becomes saturated, it passes in
second vessel and there dissolves. When all the acid has been adde
may be applied to the flask by a charcoal chauffer, until its contents
nearly dry, and the evolution of gas almost ceases, when the proce
be stopped. As much heat is given out during the condensation of t
it is necessary to surround the condensing-vessel with cold water.

The simple wash-bottle figured in the drawing will be found an e
ingly useful contrivance in a great number of chemical operations. It
in the present, and in many similar cases, to retain any liquid or solid
mechanically carried over with the gas, and it may be always employe
gas of any kind is to be passed through an alkaline or other solution
open tube dipping into the liquid prevents the possibility of absorpt
which a partial vacuum would be occasioned, and the liquid of the
vessel lost by being driven into the first.

The arrangement by which the acid is introduced, also deserves a mo
notice. The tube is bent twice upon itself, and a bulb blown in one p
(Fig. 107.) *Liquid* poured into the funnel rises upon the opposite

first bend until it reaches the second; it then flows over and runs into flask. Any quantity can then be got into the latter without the oduction of air, and without the escape of gas from the inte- . The funnel acts also as a kind of safety-valve, and in both ctions; for if by any chance the delivery-tube should be stopped the issue of gas prevented, its increased elastic force soon drives little column of liquid out of the tube, the gas escapes, and the iel is saved. On the other hand, any absorption within is quickly pensated by the entrance of air through the liquid in the bulb. plan employed on the great scale by the manufacturer is the e in principle as that described; he merely substitutes a large cylinder for the flask, and vessels of stone-ware for those of s.

Fig. 107.

'ure solution of hydrochloric acid is transparent and colourless; n strong, it fumes in the air by disengaging a little gas. It es no residue on evaporation, and gives no precipitate or milki- s with solution of chloride of barium. When saturated with the , it has a specific gravity of 1·21, and contains about 42 per cent. eal acid. The commercial acid has usually a yellow colour, and ery impure, containing salts, sulphuric acid, chloride of iron, and anic matter. It may be rendered sufficiently good for most pur- es by diluting it to the density of 1·1, which happens when the strong l is mixed with its own bulk or rather less of water, and then distilling it retort furnished with a Liebig's condenser.

mixture of nitric and hydrochloric acids has long been known under the e of *aqua regia*, from its property of dissolving gold. When these two stances are heated together, they both undergo decomposition, hyponitric l and chlorine being evolved. This at least appears to be the final result the action; at a certain stage, however, two peculiar substances, con- ing of nitrogen, oxygen, and chlorine, (chlorohyponitric acid[1] and chlo- itrous acid,[2]) appear to be formed. It is chiefly the chlorine which cks the metal.

'he presence of hydrochloric acid, or any other soluble chloride, is easily ected by solution of nitrate of silver. A white curdy precipitate is pro- ed, insoluble in nitric acid, freely soluble in ammonia, and subject to ken by exposure to light.

Compounds of Chlorine and Oxygen.

lthough these bodies never combine directly, they may be made to unite circuitous means in five different proportions, as below:—

	Composition by weight. Chlorine.	Oxygen.
Hypochlorous acid	35·5	8
Chlorous acid	35·5	24
Hypochloric acid	35·5	32
Chloric acid	35·5	40
Perchloric acid[3]	35·5	56

[ypochlorous and chloric acids are generated by the action of chlorine on ain metallic oxides; the former in the cold, the latter at a high tempe-

[1] $NO_3\,Cl_2$. [2] NO_2Cl.

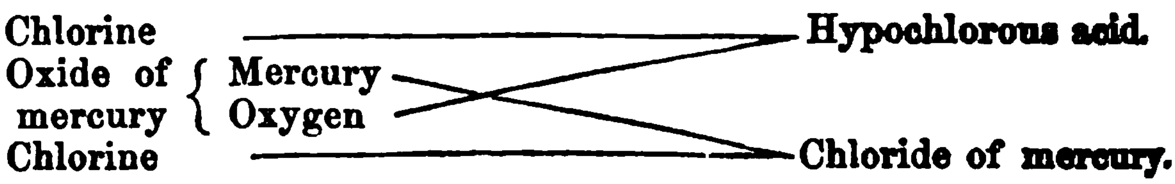
[3] Hypochlorous acid .... ClO
Chlorous acid .... ClO_3
Hypochloric acid .... ClO_4
Chloric acid .... ClO_5
Perchloric acid .... ClO_7

rature. Chlorous, hypochloric, and perchloric acids result from the decomposition of chloric acids.

Hypochlorous Acid. — This is best prepared by the action of chlorine gas upon red oxide of mercury. It is a pale yellow gaseous body, containing, in every two measures, two measures of chlorine and one of oxygen. It is very freely soluble in water, and explodes, although with no great violence, by slight elevation of temperature. The odour of this gas is peculiar, and but remotely resembles that of chlorine. It bleaches powerfully, and acts upon certain of the metals in a manner which is determined by their respective attractions for oxygen and chlorine. It forms with the alkalis a series of bleaching salts.

The preparations called *chloride of*, or *chlorinated lime* and *soda*, contain hypochlorous acid. A description of these will be found under the head of Salts of Lime.

The reaction by which hypochlorous acid is produced may thus be illustrated: —



The chloride of mercury, however, does not remain as such; it combines with another portion of the oxide, when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury.[1]

Chlorous Acid. — This substance is prepared by heating in a flask filled to the neck, a mixture of 4 parts of chlorate of potassa and 8 parts of arsenious acid with 12 parts of nitric acid previously diluted by 4 parts of water. During the operation, which must be performed in a water-bath, a greenish yellow gas is evolved, which is sparingly soluble in water, and cannot be condensed by exposure to a freezing mixture. It slowly combines with bases, producing a class of salts called chlorites. The process which gives rise to chlorous acid is rather complicated. The arsenious acid deprives the nitric acid of part of its oxygen, reducing it into nitrous acid, which is oxidized again at the expense of the chloric acid. This, by the loss of two-fifths of its oxygen, becomes chlorous acid.

Hypochloric Acid; Peroxide of Chlorine.—Chlorate of potassa is made into a paste with concentrated sulphuric acid, and cooled; this is introduced into a small glass retort, and very cautiously heated by warm water; a deep yellow gas is evolved, which is the body in question; it can be collected only by displacement, since mercury decomposes, and water absorbs the gas.

Hypochloric acid has a powerful odour, quite different from that of the preceding compounds, and of chlorine itself. It is exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling point of water. Its preparation is, therefore, always attended by danger, and should be performed only on a small scale. It is composed by measure of one volume of chlorine and two volumes of oxygen, con-

[1] A very commodious method of preparing hypochlorous acid has lately been described by M. Pelouze. Red oxide of mercury, prepared by precipitation and dried by exposure to a strong heat, is introduced into a glass tube, kept cool, and well washed, and dry chlorine gas is slowly passed over it. Chloride of mercury and hypochlorous acid are formed; the latter is collected by displacement. When the flask or bottle in which the gas is received is exposed to artificial cold by the aid of a mixture of ice and salt, the hypochlorous acid condenses to a deep red liquid, slowly soluble in water, and very subject to explosion. It is remarkable that the *crystalline* oxide of mercury prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.—*Ann. Chim. et Phys.* 3d series, vii. 179

ensed into two volumes.[1] It may be liquefied by cold. The solution of the as in water bleaches. Salts of this acid have not yet been obtained.

The *euchlorine* of Davy, prepared by gently heating chlorate of potassa ith dilute hydrochloric acid, is probably a mixture of chlorous acid and ree chlorine.

The production of chlorous acid from chlorate of potassa and sulphuric cid, depends upon the spontaneous splitting of the chloric acid into chlorous cid and perchloric acid, which latter remains in union with the potassa.[2]

When a mixture of chlorate of potassa and sugar is touched with a drop f oil of vitriol, it is instantly set on fire; the hypochloric acid disengaged eing decomposed by the combustible substance with uch violence as to cause inflammation. If crystals f chlorate of potassa be thrown into a glass of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water by the assistance of the oxygen of the hypochloric acid disengaged. Fig. 108. The liquid at the same time becomes yellow, and acquires the odour of that gas.

Fig. 108.

Chloric Acid. — This is the most important compound of the series. When chlorine is passed to saturation into a moderately strong hot solution of caustic potassa, or the carbonate of that base, and the liquid concentrated by evaporation, it furnishes, on cooling, flat tubular crystals of a colourless salt, consisting of potassa combined with chloric acid. The mother-liquor contains chloride of potassium. In this reaction a part of the potassa is decomposed; its oxygen combines with one portion of chlorine to form chloric acid, while the potassium is taken up by a second portion of the same substance.[3]

From chlorate of potassa, chloric acid may be obtained by boiling the salt with a solution of hydrofluosilicic acid, which forms an almost insoluble salt with potassa, decanting the clear liquid, and digesting it with a little silica, which removes the excess of the hydrofluosilicic acid. Filtration hrough paper must be avoided.

By cautious evaporation, the acid may be so far concentrated as to assume a syrupy consistence; it is then very easily decomposed. It sometimes sets ire to paper, or other dry organic matter, in consequence of the facility with which it is deoxidized by combustible bodies.

The chlorates are easily recognized; they give no precipitate when in olution with nitrate of baryta or silver; they evolve pure oxygen when eated, passing thereby into chlorides; and they afford, when treated with ulphuric acid, the characteristic explosive yellow gas already described. he dilute solution of the acid has no bleaching power.

Perchloric Acid.—Prof. Penny has shown that when powdered chlorate of otassa is thrown by small portions into hot nitric acid, a change of the

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[1] In equivalents, as already stated, ClO_4.

[2] 3 equiv. chloric acid { 2 eq. chlorine, 8 eq. oxygen → 2 eq. hypochloric acid.
7 eq. oxygen, 1 eq. chlorine → 1 eq. perchloric acid.

[3] 6 eq. chlorine { 5 eq. chlorine, 1 eq. chlorine; 6 eq. potassa { 5 eq. potassium, 5 eq. oxygen, 1 eq. potassa.
5 eq. chlorine, 5 eq. potassium → 5 eq. chloride potassium.
1 eq. chlorine, 5 eq. oxygen, 1 eq. potassa → 1 eq. chlorate potassa.

Iodic acid is a very soluble substance; it crystallizes in colourless, six-sided tables, which contain water. It is decomposed by heat, and its solution readily deoxidized by sulphurous acid. The iodates much resemble the chlorates; that of potassa is decomposed by heat into iodide of potassium and oxygen gas.

Periodic Acid.—When solution of iodate of soda is mixed with caustic soda, and a current of chlorine transmitted through the liquid, two salts are formed, namely, chloride of sodium and a combination of periodate of soda with hydrate of soda, which is sparingly soluble. This is separated, converted into a silver-salt, and dissolved in nitric acid; the solution yields on evaporation crystals of yellow periodate of silver; from which the acid may be separated by the action of water, which resolves the salt into free acid and insoluble basic periodate.

The acid itself may be obtained in crystals. It is permanent in the air, and capable of being resolved into iodine and oxygen by a high temperature.

BROMINE.

Bromine[1] dates back to 1826 only, having been discovered by M. Balard of Montpelier. It is found in sea-water, and is a frequent constituent of saline springs, chiefly as bromide of magnesium;—a celebrated spring of the kind exists near Kreuznach in Prussia. Bromine may be obtained pure by the following process, which depends upon the fact, that ether agitated with an aqueous solution of bromine, removes the greater part of that substance.

The mother-liquor, from which the less soluble salts have separated by crystallization, is exposed to a stream of chlorine, and then shaken up with a quantity of ether; the chlorine decomposes the bromide of magnesium, and the ether dissolves the bromine thus set free. On standing, the ethereal solution, having a fine red colour, separates, and may be removed by a funnel or pipette. Caustic potassa is then added in excess, and heat applied; bromide of potassium and bromate of potassa are formed. The solution is evaporated to dryness, and the saline matter, after ignition to redness to decompose the bromate of potassa, heated in a small retort with binoxide of manganese and sulphuric acid diluted with a little water, the neck of the retort being plunged into cold water. The bromine volatilizes in the form of a deep red vapour, which condenses into drops beneath the liquid.

Bromine is at common temperatures a red thin liquid of an exceedingly intense colour, and very volatile; it freezes at about 19° (—7°·2C), and boils at 145°·4 (63°C). The density of the liquid is 2·976, and that of the vapour 5·39. The odour of bromine is very suffocating and offensive, much resembling that of iodine, but more disagreeable. It is slightly soluble in water, more freely in alcohol, and most abundantly in ether. The aqueous solution bleaches.

Hydrobromic Acid.—This substance bears the closest resemblance in every particular to hydriodic acid; it has the same constitution by volume, very nearly the same properties, and may be prepared by means exactly similar, substituting the one body for the other. The solution of hydrobromic acid has also the power of dissolving a large quantity of bromine, thereby acquiring a red tint. Hydrobromic acid contains by weight 80 parts bromine, and 1 part hydrogen.

Bromic Acid.—Caustic alkalis in presence of bromine undergo the same change as with chlorine, bromide of the metal and bromate of the oxide being produced; these may often be separated by the inferior solubility of

[1] *From* βρῶμος, a noisome smell: a very appropriate term.

the latter. Bromic acid, obtained from bromate of baryta, closely resembles chloric acid; it is easily decomposed. The bromates when heated lose oxygen and become bromides.

No other compound of bromine and oxygen has yet been described.

FLUORINE

This element has never been isolated, at least in a state fit for examination; its properties are consequently in great measure unknown; from the observations made, it is presumed to be gaseous, and to possess colour, like chlorine. The compounds containing fluorine can be easily decomposed, and the element transferred from one body to another; but its extraordinary chemical energies towards the metals and towards silicium, a component of glass, have hitherto baffled all attempts to obtain it pure in a separate state. As fluoride of calcium it exists in small quantities in many animal substances; such as bones. Several chemists have endeavoured to obtain it by decomposing fluoride of silver by means of chlorine in vessels of fluor-spar, but even these experiments have not led to a decisive result.

Hydrofluoric Acid.—When powdered fluoride of calcium (fluor-spar) is heated with concentrated sulphuric acid in a retort of platinum or lead connected with a carefully cooled receiver of the same metal, a very volatile colourless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This was formerly believed to be the acid in an anhydrous state. M. Louyet, however, states that it still contains water, and that hydrofluoric acid, like hydrochloric acid, when anhydrous, is a gas.

When hydrofluoric acid is put into water, it unites with the latter with great violence; the dilute solution attacks glass with great facility. The concentrated acid dropped upon the skin occasions deep and malignant ulcers, so that great care is requisite in its management. Hydrofluoric acid contains 19 parts fluorine and 1 part hydrogen.

In a diluted state, this acid is occasionally used in the analysis of siliceous minerals, when alkali is to be estimated; it is employed also for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapour of the acid is also very advantageously applied to the same object in the following manner: the glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument. A shallow basin made by beating up a piece of sheet lead is then prepared, a little powdered fluor-spar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downwards, and gentle heat applied beneath, which speedily disengages the vapour of hydrofluoric acid. In a very few minutes the operation is complete; the glass is then removed and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clear and smooth.

No combination of fluorine and oxygen has yet been discovered.

SILICIUM.

Silicium, sometimes called silicon, in union with oxygen constituting silica, or the earth of flints, is a very abundant substance, and one of great importance. It enters largely into the composition of many of the rocks and mineral masses of which the surface of the earth is composed. The following process yields silicium most readily. The double fluoride of silicium and potassium is heated in a glass tube with nearly its own weight of metallic potassium; violent reaction ensues, and silicium is set free. When cold, the contents of the tube are put into cold water, which removes the saline

Glassy boracic acid in a state of fusion requires for its dissipation in vapour a very intense and long-continued heat; the solution in water cannot, however, be evaporated without very appreciable loss by volatilization; hence it is probable that the hydrate is far more volatile than the acid itself.

By heating in a glass flask or retort one part of the vitrified boracic acid, 2 of fluor-spar, and 12 of oil of vitriol, a gaseous fluoride of boron may be obtained, and received in glass jars standing over mercury. It is a transparent gas, very soluble in water, and very heavy; it forms a dense fume in the air like the fluoride of silicium.[1]

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[1] These two bodies are thus constituted: — SiF_3, and BF_3.

ON CERTAIN IMPORTANT COMPOUNDS FORMED BY THE UNION OF THE PRECEDING ELEMENTS AMONG THEMSELVES.

COMPOUNDS OF CARBON AND HYDROGEN.

THE compounds of carbon and hydrogen already known are exceedingly numerous; perhaps all, in strictness, belong to the domain of organic chemistry, as they cannot be formed by the direct union of their elements, but always arise from the decomposition of a complex body of organic origin. It will be found convenient, notwithstanding, to describe two of them in this part of the volume, as they very well illustrate the important subjects of combustion, and the nature of flame.

Light Carbonetted or Carburetted Hydrogen; Marsh-gas; Fire-damp; Gas of the Acetates.—This gas is but too often found to be abundantly disengaged in coal-mines from the fresh-cut surface of the coal, and from remarkable apertures or "blowers," which emit for a great length of time a copious stream or jet of gas, which probably existed in a state of compression, pent up in the coal.

The mud at the bottom of pools in which water-plants grow, on being stirred, suffers bubbles of gas to escape, which may be easily collected. This, on examination, is found to be chiefly a mixture of light carbonetted hydrogen and carbonic acid; the latter is easily absorbed by lime-water or caustic potassa.

Until recently, no method was known by which the gas in question could be produced in a state approaching to purity by artificial means; the various illuminating gases from pit-coal and oil, and that obtained by passing the vapour of alcohol through a red-hot tube, contain large quantities of light carbonetted hydrogen, associated, however, with other substances which hardly admit of separation. M. Dumas was so fortunate as to discover a method by which that gas can be produced at will, perfectly pure, and in any quantity.

A mixture is made of 40 parts crystallized acetate of soda, 40 parts solid hydrate of potassa, and 60 parts quicklime in powder. This mixture is transferred to a flask or retort, and strongly heated; the gas is disengaged in great abundance, and may be received over water.[1]

Light carbonetted hydrogen is a colourless and nearly inodorous gas, which does not affect vegetable colours. It burns with a yellow flame, generating

[1] Ann. Chim. et Phys. lxxiii. 93. The reaction consists in the conversion of the acetic acid, by the aid of the elements of water, into carbonic acid and light carbonetted hydrogen; the instability of the organic acid at a high temperature, and the attraction of the potassa for carbonic acid, being the determining causes. The lime prevents the hydrate of potassa from fusing and attacking the glass vessels. This decomposition is best understood by putting it in the shape of an equation.

$$\left.\begin{array}{ll}\text{Acetic acid} & C_4H_3O_3 \\ \text{Water} & HO \\ \hline & C_4H_4O_4.\end{array}\right\} = \left\{\begin{array}{ll}\text{Carbonic acid, 2 eq.} & C_2\ \ O_4. \\ \text{Marsh-gas, 2 eq.} & C_2H_4 \\ \hline & C_4H_4O_4.\end{array}\right.$$

carbonic acid and water. It is not poisonous, and may be respired to a great extent without apparent injury. The density of this compound is about 0·559, 100 cubic inches weighing 17·41 grains; and it contains carbon and hydrogen associated in the proportion of 6 parts by weight of the former to 2 of the latter.[1]

When 100 measures of this gas are mixed with 200 of pure oxygen in the eudiometer, and the mixture exploded by the electric spark, 100 measures of a gas remain which is entirely absorbable by a little solution of caustic potassa. Now carbonic acid contains its own volume of oxygen; hence one-half of the oxygen added, that is, 100 measures, must have been consumed in uniting with the hydrogen. Consequently, the gas must contain twice its own measure of hydrogen, and enough carbon to produce, when completely burned, an equal quantity of carbonic acid.

When chlorine is mixed with light carbonetted hydrogen over water, no change follows, provided light be excluded. The presence of light, however, brings about decomposition, hydrochloric acid, carbonic acid, and sometimes other products being produced. It is important to remember that the gas is not acted upon by chlorine in the dark.

Olefiant Gas.—Strong spirit of wine is mixed with five or six times its weight of oil of vitriol in a glass-flask, the tube of which passes into a wash-bottle containing caustic potassa. A second wash-bottle, partly filled with oil of vitriol, is connected to the first, and furnished with a tube dipping into the water of the pneumatic trough. On the first application of heat to the contents of the flask, alcohol, and afterwards ether, make their appearance; but, as the temperature rises, and the mixture blackens, the ether-vapour diminishes in quantity, and its place becomes in great part supplied by a permanent inflammable gas; carbonic acid and sulphurous acid are also generated at the same time, besides traces of other products. The two last-mentioned gases are absorbed by the alkali in the first bottle, and the ether vapour by the acid in the second, so that the olefiant gas is delivered tolerably pure. The reaction is too complex to be discussed at the present moment; it will be found fully described in another part of the volume. Olefiant gas thus produced is colourless, neutral, and but slightly soluble in water. Alcohol, ether, oil of turpentine, and even olive oil, as Mr. Faraday has observed, dissolve it to a considerable extent.[2] It has a faint odour of garlic. On the approach of a kindled taper it takes fire, and burns with a splendid white light, far surpassing in brilliancy that produced by light carbonetted hydrogen. This gas, when mixed with oxygen and fired, explodes with extreme violence. Its density is 0·981; 100 cubic inches weigh 30·57 grains.

By the use of the eudiometer, as already described, it has been found that each measure of olefiant gas requires for complete combustion exactly three of oxygen, and produces under these circumstances two measures of carbonic acid. Whence it is evident that it contains twice its own volume of hydrogen, combined with twice as much carbon as in marsh-gas.

By weight, these proportions will be 12 parts carbon, and 2 parts hydrogen.

Olefiant gas is decomposed by passing through a tube heated to bright redness; a deposit of charcoal takes place, and the gas becomes converted

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[1] The two carbides of hydrogen here described are thus represented in equivalents:—

Light carbonetted hydrogen	$C H_2$
Olefiant gas	C_2H_2

[2] Olefiant gas, by pressure and intense cold, produced by the evaporation in a vacuum of solid carbonic acid and ether, is condensed into a colourless transparent liquid, but not frozen. (*Faraday.*)—*R. B.*

into light carbonetted hydrogen, or even into free hydrogen, if the temperature be very high. This latter change is of course attended by increase of volume.

Chlorine acts upon olefiant gas in a very remarkable manner. When the two bodies are mixed, even in the dark, they combine in equal measures, and give rise to a heavy oily liquid, of sweetish taste and ethereal odour, to which the name chloride of hydrocarbon, or Dutch liquid, is given. It is from this peculiarity that the term *olefiant* is derived.

A pleasing and instructive experiment may also be made by mixing in a tall jar two measures of chlorine and one of olefiant gas, and then quickly applying a light to the mouth of the vessel. The chlorine and hydrogen unite with flame, which passes quickly down the jar, while the whole of the carbon is set free in the form of a thick black smoke.

Coal and Oil Gases.—The manufacture of coal-gas is at the present moment a branch of industry of great interest and importance in several points of view. The process is one of great simplicity of principle, but requires, in practice, some delicacy of management to yield a good result.

When pit-coal is subjected to destructive distillation, a variety of products show themselves; permanent gases, steam, and volatile oils, besides a not inconsiderable quantity of ammonia from the nitrogen always present in the coal. These substances vary very much in their proportions with the temperature at which the process is conducted, the permanent gases becoming more abundant with increased heat, but at the same time losing much of their value for the purposes of illumination.

The coal is distilled in cast-iron retorts, maintained at a bright red heat, and the volatilized products conducted into a long horizontal pipe of large dimensions, always half filled with liquid, into which dips the extremity of each separate tube; this is called the hydraulic main. The gas and its accompanying vapours are next made to traverse a refrigerator, usually a series of iron pipes, cooled on the outside by a stream of water; here the condensation of the tar and ammoniacal liquid becomes complete, and the gas proceeds onwards to another part of the apparatus, in which it is to be deprived of the sulphuretted hydrogen and carbonic acid gases always present in the crude product. This is generally effected by hydrate of lime, which readily absorbs the compounds in question. The purifiers are large iron vessels, partly filled with a mixture of hydrate of lime and water, in which a churning machine or agitator is kept in constant motion to prevent the subsidence of the lime. The gas is admitted at the bottom of the vessel by a great number of minute apertures, and is thus made to present a large surface of contact to the purifying liquid. The last part of the operation, which indeed is often omitted, consists in passing the gas through dilute sulphuric acid, in order to remove ammonia. The quantity thus separated is very small, relatively to the bulk of the gas, but in an extensive work becomes an object of importance.

Coal-gas thus manufactured and purified is preserved for use in immense cylindrical receivers, close at the top, suspended in tanks of water by chains to which counterpoises are attached, so that the gas-holders rise and sink in the liquid as they become filled from the purifiers or emptied by the mains. These latter are made of large diameter, to diminish as much as possible the resistance experienced by the gas in passing through such a length of pipe. The joints of these mains are yet made in such an imperfect manner, that immense loss is experienced by leakage when the pressure upon the gas at the works exceeds that exerted by a column of water an inch in height.[1]

[1] It may give some idea of the extent of this species of manufacture, to mention, that in the year 1838, for lighting London and the suburbs alone, there were eighteen public gas works, and £2,800,000 invested in pipes and apparatus. The yearly revenue amounted to

Coal-gas varies much in composition, judging from its variable density and illuminating power, and from the analyses which have been made. The difficulties of such investigations are very great, and unless particular precaution be taken, the results are merely approximative. The purified gas is believed to contain the following substances, of which the first is most abundant, and the second most valuable.

Light carbonetted hydrogen.
Olefiant gas.
Hydrogen.
Carbonic oxide.
Nitrogen.
Vapours of volatile liquid carbides of hydrogen.[1]
Vapour of bisulphide of carbon.

Separated by Condensation and by the Purifiers.

Tar and volatile oils.
Sulphate of ammonia, chloride and sulphide of ammonium.
Sulphuretted hydrogen.
Carbonic acid.
Hydrocyanic acid, or cyanide of ammonium.

A very far better illuminating gas may be prepared from oil, by dropping it into a red-hot iron retort filled with coke; the liquid is in great part decomposed and converted into permanent gas, which requires no purification, as it is quite free from the ammoniacal and sulphur compounds which vitiate the gas from coal. A few years ago this article was prepared in London; it was compressed for the use of the consumer into strong iron vessels, to the extent of 30 atmospheres; these were furnished with a screw-valve of peculiar construction, and exchanged for others when exhausted. The comparative high price of the material, and other circumstances, led to the abandonment of the undertaking.

COMBUSTION, AND THE STRUCTURE OF FLAME.

When any solid substance, capable of bearing the fire, is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus, a bar of platinum or a piece of porcelain raised to a particular temperature, become what is called red-hot, or emissive of red light; at a higher degree of heat this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxy-hydrogen blowpipe, the light becomes exceedingly powerful and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited.*

Again, if the same experiment be made on a piece of charcoal, similar effects will be observed, but something in addition; for whereas the platinum or porcelain, when removed from the fire, or the lime from the blow-pipe flame, begin immediately to cool, and emit less and less light, until they become completely obscure, the charcoal maintains to a great extent its high temperature. Unlike the other bodies too, which suffer no change whatever either of weight or substance, the charcoal gradually wastes away until it

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£450,000, and the consumption of coal in the same period to 180,000 tons, 1,460 *millions* of cubic feet of gas being made in the year. There were 134,300 private lights, and 30,400 street lamps. 890 tons of coal were used in the retorts in the space of twenty-four hours at mid-winter, and 7,120,000 cubic feet of gas consumed in the longest night.—Dr. Ure, Dictionary of Arts and Manufactures. Since that time the production of gas has been very considerably increased.

[1] These bodies increase the illuminating power, and confer on the gas its peculiar odour.

ppears. This is what is called *combustion* in contradistinction to mere ion; the charcoal burns, and its temperature is kept up by the heat red in the act of union with the oxygen of the air.

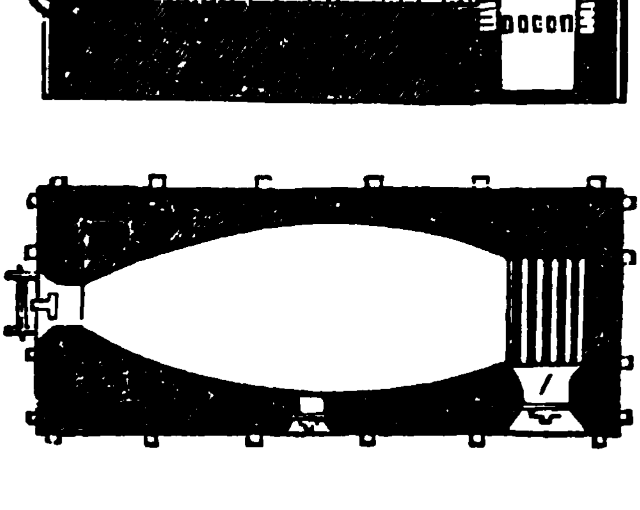
the most general sense, a body in a state of combustion is one in the f undergoing intense chemical action: any chemical action whatsoever, energy rise sufficiently high, may produce the phenomenon of combion, by *heating the body to such an extent that it becomes luminous.*

all ordinary cases of combustion, the action lies between the burning and the oxygen of the air; and since the materials employed for the omical production of heat and light consist of carbon chiefly, or that tance conjoined with a certain proportion of hydrogen and oxygen, all non effects of this nature are cases of the rapid and violent oxidation arbon and hydrogen by the aid of the free oxygen of the air. The heat t be referred to the act of chemical union, and the light to the elevated perature.

y this principle it is easy to understand the means which must be adopted crease the heat of ordinary fires to the point necessary to melt refrac-metals, and to bring about certain desired effects of chemical decomtion. If the rate of consumption of the fuel can be increased by a more d introduction of air into the burning mass, the intensity of the heat of necessity rise in the same ratio, there being reason to believe that the ntity of heat evolved is fixed and definite for the same constant quantity hemical action. This increased supply of air may be effected by two inct methods; it may be forced into the fire by bellows or blowing-hines, as in the common forge, and in the blast and cupola-furnaces of iron-worker, or it may be drawn through the burning materials by the of a tall chimney, the fire-place being closed on all sides, and no ence of air allowed, save between the bars of the grate. Such is the kind urnace generally employed by the scientific chemist in assaying and in reduction of metallic oxides by charcoal; the principle will be at once erstood by the aid of the sectional drawing, in which a crucible is repreted, arranged in the fire for an operation of the kind mentioned. . 111.)

Fig. 111.

Fig. 112

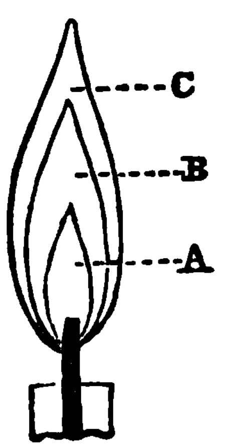


The "reverberatory" furnace (fig. 112) is one very much used in the arts when substances are to be exposed to heat without contact with the fuel. The fire-chamber is separated from the bed or hearth of the furnace by a low wall or *bridge* of brick-work, and the flame and heated air are reflected downwards by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind, from the temperature of dull redness, to that required to melt very large quantities of cast-iron. The fire is urged by a chimney provided with a sliding-plate or damper to regulate the draught.

Solids and liquids, as melted metal, enjoy, when sufficiently heated, the faculty of emitting light; the same power is possessed by gaseous bodies, but the temperature required to render a gas luminous is incomparably higher than in the cases already described. Gas or vapour in this condition constitutes *flame*, the actual temperature of which generally exceeds that of the white heat of solid bodies.

The light emitted from pure flame is exceedingly feeble; illuminating power is almost entirely dependent upon the presence of solid matter. The flame of hydrogen, or of the mixed gases, is scarcely visible in full daylight; in a dusty atmosphere, however, it becomes much more luminous by igniting to intense whiteness the floating particles with which it comes in contact. The piece of lime in the blowpipe flame cannot have a higher temperature than that of the flame itself; yet the light it throws off is infinitely greater.

Fig. 113.



Flames burning in the air, and not supplied with oxygen from another source, are, as already stated, hollow; the chemical action is necessarily confined to the spot where the two bodies unite. That of a lamp or candle, when carefully examined, is seen to consist of three separate portions. The dark central part, A, fig. 113, easily rendered evident by depressing upon the flame a piece of fine wire-gauze, consists of combustible matter drawn up by the capillarity of the wick, and volatilized by the heat. This is surrounded by a highly luminous cone or envelope, B, which, in contact with a cold body, deposits soot. On the outside a second cone, C, is to be traced, feeble in its light-giving power, but having an exceedingly high temperature. The explanation of these appearances is easy: carbon and hydrogen are very unequal in their attraction for oxygen, the latter greatly exceeding the former in this respect; consequently, when both are present, and the supply of oxygen limited, the hydrogen takes all, to the exclusion of a great part of the carbon. Now this happens in the case under consideration, at some little distance within the outer surface of the flame, namely, in the luminous portion; the little oxygen which has penetrated thus far inwards is entirely consumed by the hydrogen, and the particles of deposited charcoal, which would, were they cooler, form smoke, become intensely ignited by the burning hydrogen, and evolve a light whose whiteness marks a very elevated temperature. In the exterior and scarcely visible cone, these particles of carbon undergo combustion.

A jet of coal-gas exhibits these phenomena; but, if the gas be previously mingled with air, or if air be forcibly mixed with, or driven into the flame, no such separation of carbon occurs, the hydrogen and carbon burn *together*, and the illuminating power almost disappears.

The common mouth blowpipe is a little instrument of high utility; it is merely a brass tube, fitted with an ivory mouth-piece, and terminated by a jet, having a small aperture by which a current of air is driven across the flame of a candle. The best form is perhaps that contrived by Mr. Pepys, and shown in fig. 114. The flame so produced is very peculiar.

Instead of the double envelope just described, two long pointed cones are

, which, when the blowpipe is good, and ture smooth and round, are very well de- outer one being yellowish, and the inner ig. 115. A double combustion is, in fact, , by the blast in the inside, and by the air. The space between the inner and nes is filled with exceedingly hot com- matter, possessing strong reducing or ing powers, while the highly heated air ond the point of the exterior cone ox- ith great facility. A small portion of supported on a piece of charcoal, or a ring at the end of a fine platinum thus in an instant be exposed to a very ree of heat under these contrasted cir- ces, and observations of great value made short time. The use of the instrument an even and uninterrupted blast of ration, by a method easily acquired with patience; it consists in employing for pose the muscles of the cheeks alone, on being conducted through the nostrils, mouth from time to time replenished without intermission of the blast.

Fig. 114.

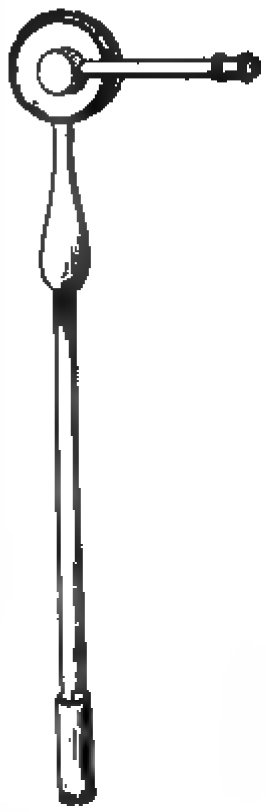
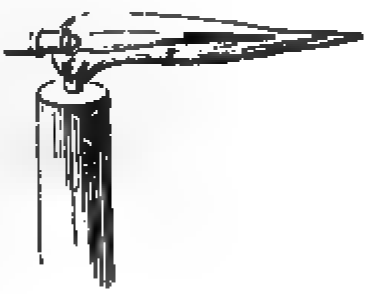


Fig. 115.



rgand lamp, adapted to burn either oil t, but especially the latter, is a very piece of chemical apparatus. In this e wick is cylindrical, the flame being with air both inside and outside; the ion is greatly aided by the chimney, made of copper when the lamp is used rce of heat. Fig. 116 exhibits, in sec- excellent lamp of this kind for burning or wood-spirit. It is constructed of thin and furnished with ground caps to the der and aperture[1] by which the spirit is ed, in order to prevent loss when the not in use. Glass spirit-lamps, fitted

Fig. 116.

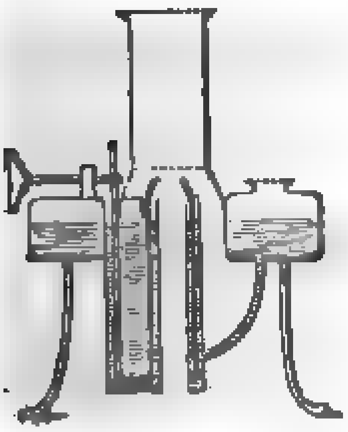


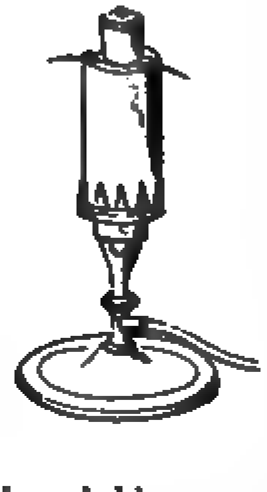
Fig. 117.

[1] in use this *aperture must always* be open, otherwise an accident is sure to happen, expands *the air in the lamp,* and the spirit is forced out in a state of inflammation.

with caps (fig. 117) to prevent evaporation, are very convenient for occasional use, being always ready and in order.[1]

In London, and other large towns where coal-gas is to be had, that substance is constantly used with the greatest economy and advantage in every respect as a source of heat. Retorts, flasks, capsules, and other vessels, can be thus exposed to an easily regulated and invariable temperature for many successive hours. Small platinum crucibles may be ignited to redness by placing them over the flame on a little wire triangle. The arrangement shown in fig. 119, consisting of a common Argand gas-burner fixed on a heavy and low foot, and connected with a flexible tube of caoutchouc or other material, leaves nothing to desire.

Fig. 119.



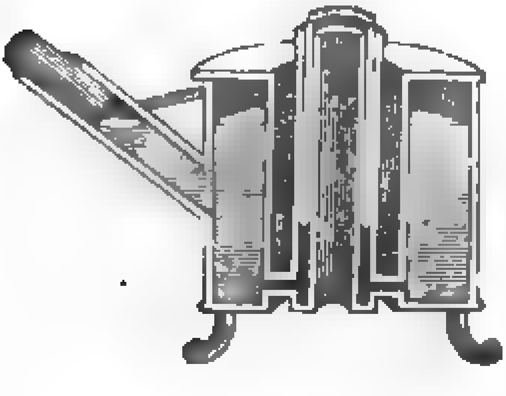
The kindling-point, or temperature at which combustion commences, is very different with different substances: phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies the same fact is observed: hydrogen is inflamed by a red-hot wire; carbonetted hydrogen requires a white heat to effect the same thing. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir H. Davy's invaluable safe-lamp.

Mention has already been made of the frequent disengagement of great quantities of light carbonetted hydrogen gas in coal-mines. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light, and burning with a pale blue flame; and many fearful accidents have occurred from the ignition of large quantities of mixed air and gas occupying the extensive galleries and workingh of a mine. Sir H. Davy undertook an investigation with a view to discover some remedy for this constantly-occurring calamity; his labours resulted in some exceedingly important discoveries respecting flame, of which the substance has been given, and which led to the construction of the lamp which bears his name.

When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one fired by the electric spark, or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

In this experiment, high conducting power and diminished diameter compensate for diminution of length; and to such an extent can this be carried,

Fig. 118.



[1] The spirit-lamp represented in fig. 118, is one contrived by Dr. Mitchell. "It is made of tinned iron. The alcohol is poured out by means of the hollow handle, and is admitted to the cylindrical burner by two or three tubes which are placed at the very bottom of the fountain. By such an arrangement of parts, the alcohol may be added as it is consumed, and the flame kept uniform, and as the pipes which pass to the burner are so remote from the flame, the alcohol never becomes heated so as to fly off through the vent-hole, and thus to cause greater waste and danger of explosion."

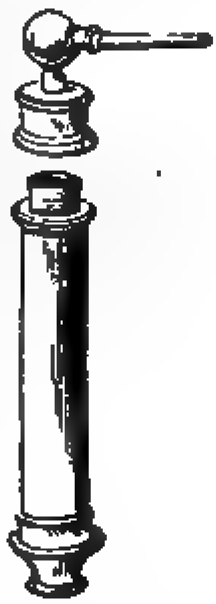
A cylindrical chimney is an advantageous addition for many purposes. It may be made of tin-plate or copper.—R. B.

etallic gauze, which may be looked upon as a series of very short tubes arranged side by side, arrests in the most complete manner the e of flame in explosive mixtures, when of sufficient of fineness, depending upon the inflammability of the Most providentially, the fire-damp mixture has an ex-gly high kindling point; a red heat does not cause in-tion; consequently, the gauze will be safe for this ice, when flame would pass in almost any other case. miner's safe-lamp (fig. 120) is merely an ordinary oil-he flame of which is enclosed in a cage of wire gauze; louble at the upper part, containing about 400 aper-o the square inch. The tube for supplying oil to the ir reaches nearly to the bottom of the latter, while the lmits of being trimmed by a bent wire passing with through a small tube in the body of the lamp; the an thus be kept burning for any length of time, with-necessity of unscrewing the cage. When this lamp is nto an explosive atmosphere, although the fire-damp rn within the cage with such energy as sometimes the metallic tissue to dull redness, the flame is not nicated to the mixture on the outside.

Fig. 120.

e effects may be conveniently studied by suspending ip in a large glass jar, and gradually admitting coal-ow. The oil-flame is at first elongated, and then, as portion of gas increases, extinguished, while the in-f the gauze cylinder becomes filled with the burn-xture of gas and air. As the atmosphere becomes the wick is once more relighted. These appear-ire so remarkable, that the lamp becomes an admi-ldicator of the state of the air in different parts of ie.[1]

Fig. 121.



same great principle has been ingeniously applied Hemming to the construction of the oxy-hydrogen jet formerly mentioned. This is a tube of brass four inches long, filled with straight pieces of fine wire, the whole being tightly wedged together by a l rod, forcibly driven into the centre of the bundle. 21. The arrangement thus presents a series of ubes, very long in proportion to their diameter, the powers of which are so great as to prevent the pos-of the passage of flame, even with oxygen and hy-. The jet may be used, as before mentioned, with non bladder, without a chance of explosion. The nental fact of flame being extinguished by contact cold body, may be elegantly shown by twisting a wire (fig. 122) into a short spiral, about 0·1 inch

Fig. 122.

Is the true use of the lamp, namely, to permit the viewer or superintendent, with to himself, to examine the state of the air in every part of the mine; not to enable n to continue their labours in an atmosphere habitually explosive, which must be r human respiration, although the evil effects may be slow to appear. Owners of es should be compelled either to adopt efficient means of ventilation, or to close s of this dangerous character altogether.

in diameter, and then passing it *cold* over the flame of a wax candle; the latter is extinguished. If the spiral be now heated to redness by a spirit-lamp, and the experiment repeated, no such effect follows.[1]

NITROGEN AND HYDROGEN; AMMONIA.

When powdered sal-ammoniac is mixed with moist hydrate of lime, and gently heated in a glass flask, a large quantity of gaseous matter is disengaged, which must be collected over mercury, or by displacement, advantage being taken of its low specific gravity.

Ammoniacal gas thus obtained is colourless; it has a very powerful pungent odour, and a strong alkaline reaction to test-paper, by which it may be at once distinguished from nearly all other bodies possessing the same physical characters. Under a pressure of 6·5 atmospheres at 60° (15°·5C), ammonia condenses to the liquid form.[2] Water dissolves about 700 times its volume of this remarkable gas, forming a solution which in a more dilute state has long been known under the name of *liquor ammoniæ;* by heat, a great part is again expelled. The solution is decomposed by chlorine, sal-ammoniac being formed, and nitrogen set free.

Ammonia has a density of 0·589; 100 cubic inches weigh 18·26 grains. It cannot be formed by the direct union of its elements, although it is sometimes produced under rather remarkable circumstances by the deoxidation of nitric acid. The great sources of ammonia are the feebly-compounded azotized principles of the animal and vegetable kingdoms, which, when left to putrefactive change, or subjected to destructive distillation, almost invariably give rise to an abundant production of this substance.

The analysis of ammoniacal gas is easily effected. When a portion is confined in a graduated tube over mercury, and electric sparks passed through it for a considerable time, the volume of the gas gradually increases until it becomes doubled. On examination, the tube is found to contain a mixture of 3 measures hydrogen gas, and 1 measure nitrogen. Every two volumes of the ammonia, therefore, contained three volumes of hydrogen and one of nitrogen, the whole being condensed to the extent of one-half. The weight of the two constituents will be in the proportion of 3 parts hydrogen to 14 parts nitrogen.

Ammonia may also be decomposed into its elements by transmission through a red-hot tube.

Solution of ammonia is a very valuable reagent, and is employed in a great number of chemical operations, for some of which it is necessary to have it perfectly pure. The best mode of preparation is the following:—

Equal weights of sal-ammoniac and quicklime are taken: the lime is slaked in a covered basin, and the salt reduced to powder. These are mixed, and introduced into the flask employed in preparing solution of hydrochloric acid, together with just enough water to damp the mixture, and cause it to aggregate into lumps; the rest of the apparatus is arranged exactly as in

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[1] Where coal-gas is to be had, it may be advantageously used as a source of heat, by taking advantage of the above-mentioned fact. On passing a current of gas through a wide vertical tube, open at the bottom to afford a free mixture with atmospheric air, but closed at the top by wire gauze, and then kindling the mixture after its escape through the meshes, it will burn with feeble illuminating power, but no loss of heat. When the proportion of the gas to the atmospheric air is such as not to allow the flame to become yellow, the combustion will be complete, and no carbonaceous deposit will be formed on cold bodies held over the flames. The length and diameter of the cylinder are determined by the amount of gas to be burnt, and the length may be much decreased by interposing a second diaphragm of wire gauze about mid-length of the cylinder, the current of gas being introduced below this, by which means a more thorough and rapid mixture is made with the atmospheric air.—Sir John Robinson, K. H. &c., Ed. New Phil. Journal, 1840.—R. B.

[2] At the temperature of −103° (−75°C), liquid ammonia freezes into a colourless solid, heavier than the liquid itself.—(Faraday.)—R. B.

rmer case, with an ounce or two of water in the wash-bottle, or enough rer the ends of the tubes, and the gas conducted afterwards into pure .ed water, artificially cooled, as before. The cork-joints are made tight wax, a little water is put into the safety-funnel, heat cautiously applied flask, and the whole left to itself. The disengagement of ammonia is regular and uniform. Chloride of calcium, with excess of hydrate of remains in the flask.[1]

e decomposition of the salt is usually represented in the manner shown e subjoined diagram.

Sal-ammoniac	Ammonia		Ammonia.
	Hydrochloric acid	Hydrogen	Water.
		Chlorine	
Lime.	Oxygen		
	Calcium		Chloride of calcium.

lution of ammonia should be perfectly colourless, leave no residue on ration, and when supersaturated by nitric acid, give no cloud or mud- with nitrate of silver. Its density diminishes with its strength, that e most concentrated being about 0·875; the value in alkali of any le of liquor ammoniæ is most safely inferred, not from a knowledge density, but from the quantity of acid a given amount will saturate. mode of conducting this experiment will be found described under *imetry*.

ien solution of ammonia is mixed with acids of various kinds, salts are ated, which resemble in the most complete manner the corresponding ounds of potassa and soda; these are best discussed in connexion with itter. Any ammoniacal salt can at once be recognized by the evolution imonia when it is heated with hydrate of lime, or solution of carbonate tassa or soda.

NITROGEN AND BORON.

combination of nitrogen with boron was first obtained by Balmain. er prepared it by mixing one part of pure dry borax with two parts of l-ammoniac, heating to redness, boiling with water and hydrochloric filtering and washing with hot water, when the compound remained in rm of a white powder. As yet it has not been obtained quite free oxygen.

SULPHUR, SELENIUM, AND PHOSPHORUS, WITH HYDROGEN.

phuretted Hydrogen; Hydrosulphuric Acid. — There are two methods by this important compound can be readily prepared, namely, by the of dilute sulphuric acid upon sulphide of iron, and by the decomposi- f sulphide of antimony by hydrochloric acid. The first method yields st easily, and the second in the purest state.

tosulphide of iron is put into the apparatus for hydrogen, already l times mentioned, together with some water, and oil of vitriol is added funnel, until a copious disengagement of gas takes place. This is to llected over tepid water. The reaction is thus explained: —

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[1] See Fig. 106, p. 142.

Sulphide of iron { Sulphur / Iron — Sulphuretted hydrogen.
Water............... { Hydrogen / Oxygen
Sulphuric acid — Sulphate of protoxide of iron.

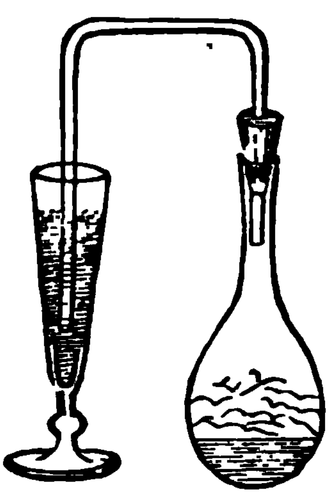
By the other plan, finely-powdered sulphide of antimony is put into a flask, to which a cork and bent tube can be adapted, and strong liquid hydrochloric acid poured upon it. On the application of heat, a double interchange occurs between the bodies present, sulphuretted hydrogen being formed, and chloride of antimony. The action only lasts while the heat is maintained.

Hydrochloric acid..... { Hydrogen / Chlorine — Sulphuretted hydrogen.
Sulphide of antimony { Sulphur / Antimony — Chloride of antimony.

Sulphuretted hydrogen is a colourless gas, having the odour of putrid eggs: it is most offensive when in small quantity, when a mere trace is present in the air. It is not irritating, but, on the contrary, powerfully narcotic. When set on fire, it burns with a blue flame, producing water and sulphurous acid when the supply of air is abundant; and depositing sulphur when the oxygen is deficient. Mixed with chlorine, it is instantly decomposed, with separation of the whole of the sulphur.

This gas has a specific gravity of 1·171; 100 cubic inches weigh 36·33 grains.

Fig. 123.



A pressure of 17 atmospheres at 50° (10°C) reduces it to the liquid form. Cold water dissolves its own volume of sulphuretted hydrogen, and the solution is often directed to be kept as a test; it is so prone to decomposition, however, by the oxygen of the air, that it speedily spoils. A much better plan is to keep a little apparatus for generating the gas always at hand, and ready for use at a moment's notice. A small bottle or flask (fig. 123), to which a bit of bent tube is fitted by a cork, is supplied with a little sulphide of iron and water; when required for use, a few drops of oil of vitriol are added, and the gas is at once evolved. The experiment completed, the liquid is poured from the bottle, replaced by a little clean water, and the instrument is again ready for use.

When potassium is heated in sulphuretted hydrogen, the metal burns with great energy, becoming converted into sulphide, while pure hydrogen remains, equal in volume to the original gas. Taking this fact into account, and comparing the density of the gas with those of hydrogen and sulphur-vapour, it appears that every volume of sulphuretted hydrogen contains one volume of hydrogen and one-sixth of a volume of sulphur-vapour, the whole condensed into one volume. This corresponds very nearly with its composition by weight, determined by other means, namely, 16 parts sulphur and 1 part hydrogen.

When a mixture is made of 100 measures of sulphuretted hydrogen and 150 measures of pure oxygen, and exploded by the electric spark, complete combustion ensues, and 100 measures of sulphurous acid gas result.

Sulphuretted hydrogen is a frequent product of the putrefaction of organic matter, both animal and vegetable; it occurs also in certain mineral springs, *as at Harrowgate*, and elsewhere. When accidentally present in the atmo-

sphere of an apartment, it may be instantaneously destroyed by a small quantity of chlorine gas.

There are few reagents of greater value to the practical chemist than this substance; when brought in contact with many metallic solutions, it gives rise to precipitates, which are often exceedingly characteristic in appearance, and it frequently affords the means also of separating metals from each other with the greatest precision and certainty. The precipitates spoken of are insoluble sulphides, formed by the mutual decomposition of the metallic oxides or chlorides and sulphuretted hydrogen, water or hydrochloric acid being produced at the same time. All the metals are, in fact, precipitated whose sulphides are insoluble in water and in dilute acids.

Sulphuretted hydrogen possesses itself the properties of an acid; its solution in water reddens litmus paper.

The best test for the presence of this compound is paper wetted with solution of acetate of lead. This salt is blackened by the smallest trace of the gas.

Persulphide of Hydrogen.—This substance corresponds in constitution and instability to the binoxide of hydrogen; it is prepared by the following means:—

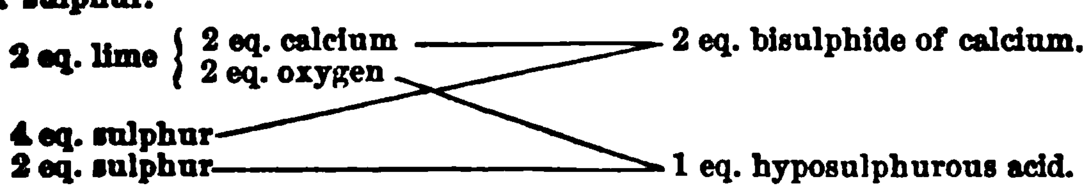
Equal weights of slaked lime and flowers of sulphur are boiled with 5 or 6 parts of water for half an hour, when a deep orange-coloured solution is produced, containing among other things persulphide of calcium. This is filtered, and slowly added to an excess of dilute sulphuric acid, with constant agitation. A white precipitate of separated sulphur and sulphate of lime makes its appearance, together with a quantity of yellow oily-looking matter, which collects at the bottom of the vessel; this is persulphide of hydrogen.[1]

If the experiment be conducted by pouring the *acid* into the solution of sulphide, then nothing but finely-divided precipitated sulphur is obtained.

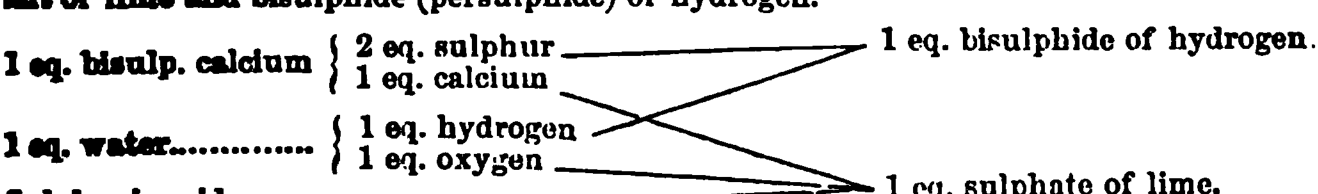
The persulphide is a yellow, viscid, insoluble liquid, exhaling the odour of sulphuretted hydrogen; its specific gravity is 1·769. It is slowly decomposed even in the cold into sulphur and sulphuretted hydrogen, and instantly by a higher temperature, or by contact with many metallic oxides. This compound probably contains twice as much sulphur in relation to the other elements, as sulphuretted hydrogen.

Hydrogen and Selenium; Seleniuretted Hydrogen.—This substance is produced by the action of dilute sulphuric acid upon selenide of potassium or iron; it very much resembles sulphuretted hydrogen, being a colourless gas, freely

[1] The reaction which ensues when hydrate of lime, sulphur, and water, are boiled together, is rather complex; bisulphide or pentasulphide of calcium being formed, together with hyposulphite of lime, arising from the transfer of the oxygen of the decomposed lime to another portion of sulphur.



The bisulphide of calcium, decomposed by an acid under favourable circumstances, yields a salt of lime and bisulphide (persulphide) of hydrogen.



When the acid is poured into the sulphide, sulphuretted hydrogen, water, and sulphate of lime, are produced, while the excess of sulphur is thrown down as a fine white powder, the "precipitated sulphur" of the *Pharmacopœia*. When the object is to prepare the latter substance, hydrochloric acid must be used in the place of sulphuric.

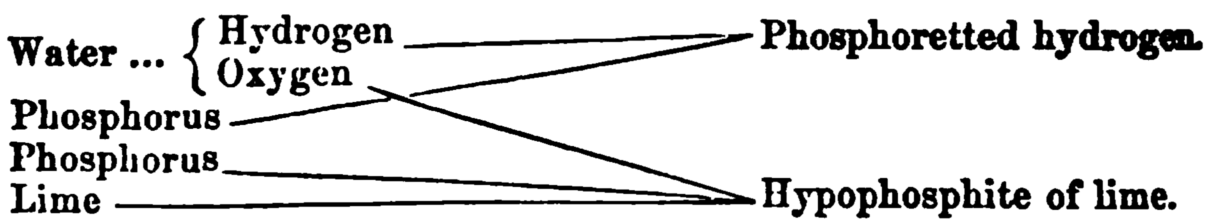
soluble in water, and decomposing metallic solutions like that substance; insoluble selenides are thus produced. This gas is said to act very powerfully upon the lining membrane of the nose, exciting catarrhal symptoms, and destroying the sense of smell. It contains 39·5 parts selenium, and 1 part hydrogen.

Phosphorus and Hydrogen; Phosphoretted Hydrogen.—This body bears a slight analogy in some of its chemical relations to ammoniacal gas; it is, however, destitute of alkaline properties.

Phosphoretted hydrogen may be obtained in a state of purity by heating in a small retort hydrated phosphorous acid, which is by such treatment decomposed into phosphoretted hydrogen and hydrated phosphoric acid.[1]

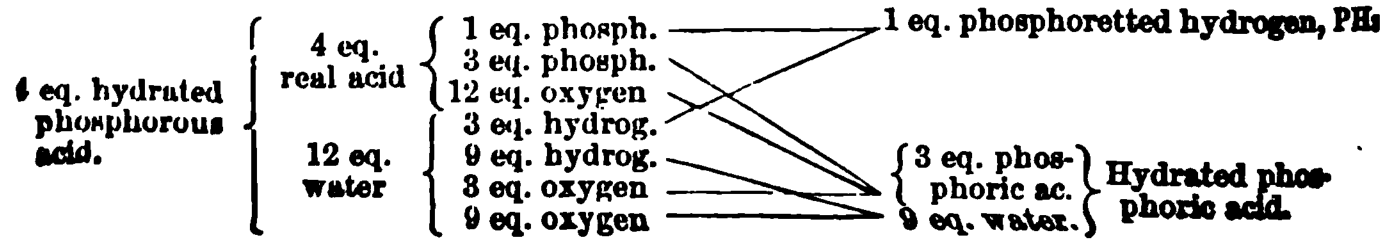
Thus obtained, the gas has a density of 1·24. It contains 32 parts phosphorus, and 3 parts hydrogen, and is so constituted that every two volumes contain 3 volumes of hydrogen and half a volume of phosphorus-vapour, condensed into two volumes. It possesses a highly disagreeable odour of garlic, is slightly soluble in water, and burns with a brilliant white flame, forming water and phosphoric acid.

Phosphoretted hydrogen may also be produced by boiling together in a retort of small dimensions caustic potassa or hydrate of lime, water, and phosphorus; the vessel should be filled to the neck, and the extremity of the latter made to dip into the water of the pneumatic trough. In the reaction which ensues the water is decomposed, and both its elements combine with the phosphorus. The alkali acts by *its presence* determining the decomposition of the water, in the same manner as sulphuric acid determines the decomposition of water when in contact with zinc.



The phosphoretted hydrogen prepared by the latter process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas; with the latter, the experiment is very beautiful, but requires caution; the bubbles should be singly admitted. When kept over water for some time, the gas loses this property, without otherwise suffering any appreciable change: but if dried by chloride of calcium, it may be kept unaltered for a much longer period. M. Paul Thénard has shown that the spontaneous combustibility of the gas arises from the presence of the vapour of a liquid phosphide of hydrogen, which can be procured in small quantity, by conveying the gas produced by the action of the water on phosphide of calcium through a tube cooled by a freezing mixture. This substance forms a colourless liquid of high refractive power and very great volatility. It does not freeze at 0° (—17°·8C). In contact with air it inflames instantly, and its vapour in very small quantity communicates spontaneous inflammability to pure phosphoretted hydrogen, and to all other combustible gases. It is decomposed by light into gaseous phosphoretted hydrogen, and a solid phosphide which is often seen on the inside of jars containing gas which has lost

[1] Decomposition of hydrated phosphorous acid by heat:—



property of spontaneous inflammation by exposure to light. Strong ids occasion its instantaneous decomposition. Its instability is equal to at of binoxide of hydrogen. It is to be observed that the pure phosphotted hydrogen gas itself becomes spontaneously inflammable if heated to e temperature of boiling water.[1]

Phosphoretted hydrogen decomposes several metallic solutions, giving rise precipitates of insoluble phosphides. With hydriodic acid it forms a crysline compound somewhat resembling sal-ammoniac.

NITROGEN WITH CHLORINE AND IODINE.

Chloride of Nitrogen.—When sal-ammoniac or nitrate of ammonia is dislved in water, and a jar of chlorine gas inverted into the solution, the gas absorbed, and a deep yellow oily liquid is observed to collect upon the rface of the solution, which ultimately sinks in globules to the bottom. his is chloride of nitrogen, the most dangerously-explosive substance known. he following is the safest method of conducting the experiment:—

A somewhat dilute and tepid solution of pure sal-ammoniac in distilled ater is poured into a clean basin, and a bottle of chlorine, the neck of hich is quite free from grease, inverted into it. A shallow and heavy leaden p is placed beneath the mouth of the bottle to collect the product. When ough has been obtained, the leaden vessel may be withdrawn with its danrous contents, the chloride remaining covered with a stratum of water. he operator should protect his face with a strong wire-gauze mask when perimenting upon this substance.

The change is explained by the following diagram:-

Chlorine ———————— Chloride of nitrogen.
Chlorine ———————— Hydrochloric acid
Sal-ammoniac { Nitrogen
Sal-ammoniac { Hydrogen
Sal-ammoniac { Hydrochloric acid ———————— Hydrochloric acid.

Chloride of nitrogen is very volatile, and its vapour is exceedingly irritag to the eyes. It has a specific gravity of 1·653. It may be distilled at 0° (71°·1C), although the experiment is attended with great danger. tween 200° (93°·3C) and 212° (100°C) it explodes with the most fearful lence. Contact with almost any combustible matter, as oil or fat of any d, determines the explosion at common temperatures; a vessel of porcein, glass, or even of cast-iron, is broken to pieces, and the leaden cup eives a deep indentation. This body has usually been supposed to contain trogen and chlorine in the proportion of 14 parts of the former to 106·5 rts of the latter, but recent experiments upon the corresponding iodinempound induce a belief that it contains hydrogen.[2]

Iodide of Nitrogen.—When finely-powdered iodine is put into caustic amnia it is in part dissolved, giving a deep brown solution, and the residue converted into a black powder, which is the substance in question The own liquid consists of hydriodic acid holding iodine in solution, and is sily separated from the solid product by a filter. The latter while still t is distributed in small quantities upon separate pieces of bibulous paper, d left to dry in the air.

Iodide of nitrogen is a black insoluble powder, which, when dry, explodes th the slightest touch, even that of a feather; and sometimes without any vious cause. The explosion is not nearly so violent as that of the com-

[1] Ann. Chim. et Phys. 3rd series, xiv. 5. According to M. Thénard, the new liquid phosphide hydrogen contains PH_2 and the solid P_2H. The gas is represented by the formula PH_3.
[2] Instead of NCl_3, it may in reality be $NH\,Cl_2$.

ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY.

THE study of the non-metallic elements can be pushed to a very considerable extent, and a large amount of precise and exceedingly important information acquired, without much direct reference to the great fundamental laws of chemical union; the subject cannot be discussed in this manner completely, as will be obvious from occasional cases of anticipation in many of the foregoing foot-notes; still, much may be done by this simple method of proceeding. The bodies themselves, in their combinations, furnish admirable illustrations of the general laws referred to, but the study of their leading characters and relations does not of necessity involve a previous knowledge of these laws themselves.

It is thought that by such an arrangement the comprehension of these very important general principles may become in some measure facilitated by constant references to examples of combinations, the elements and products of which have been already described. So much more difficult is it to gain a clear and distinct idea of any proposition of great generality from a simple enunciation, than to understand the bearing of the same law when illustrated by a single good and familiar instance.

Before proceeding farther, however, it is absolutely necessary that these matters should be discussed; the metallic compounds are so numerous and complicated, that the establishment of some general principle, some connecting link, becomes indispensable. The doctrine of equivalents, and the laws which regulate the formation of saline compounds, supply this deficiency.

In the organic department of the science, the most interesting perhaps of all, a knowledge of these principles, and, farther, an acquaintance or even familiarity with the beautiful system of chemical notation now in use, are absolutely required. This latter is found of very great service in the study of salts and other complex inorganic compounds, but in that of organic chemistry it cannot be dispensed with.

It will be proper to commence with a notice of the principles which regulate the modern nomenclature in use in chemical writings.

NOMENCLATURE.

In the early days of chemistry the arbitrary and fanciful names which were conferred by each experimenter on the new compounds he discovered sufficed to distinguish these from each other, and to render intelligible the description given of their production. Such terms as *oil of vitriol*, *spirit of salt*, *oil of tartar*, *butter of antimony*, *sugar of lead*, *flowers of zinc*, *sal enixum*, *sal mirabile*, &c., were then quite admissible. In process of time, however, when the number of known substances became vastly increased, the confusion of language produced by the want of a more systematic kind of nomenclature became quite intolerable, and the evil was still farther increased by the frequent use of numerous synonyms to designate the same substance.

In the year 1787, Lavoisier and his colleagues published the plan of the

remarkable system of nomenclature, which, with some important extensions since rendered necessary, has up to the present time to a great extent satisfied the wants of the science. It is in organic chemistry that the deficiencies of this plan are chiefly felt, and that something like a return to the old method has been rendered inevitable. Organic chemistry is an entirely new science which has sprung up since the death of these eminent men, and has to deal with bodies of a constitution or *type* differing completely from that of the inorganic acids, bases and salts which formed the subjects of the chemical studies of that period. The rapid progress of discovery, by which new compounds, and new classes of compounds, often of the most unexpected nature, are continually brought to light, sufficiently proves that the time to attempt the construction of a permanent systematic plan of naming organic bodies has not yet arrived.

The principle of the nomenclature in use may be thus explained:—Elementary substances still receive arbitrary names, generally, but not always, referring to some marked peculiarity of the body; an uniformity in the termination of the word has generally been observed, as in the case of new metals whose names are made to end in *ium*.

Compounds formed by the union of non-metallic elements with metals, or with other non-metallic elements, are collected into groups having a kind of generic name derived from the non-metallic element, or that most opposed in characters to a metal, and made to terminate in *ide*.[1] Thus we have oxides, chlorides, iodides, bromides, &c., of hydrogen and of the several metals; oxides of chlorine; chlorides of iodine and sulphur; sulphides and phosphides of hydrogen and the metals.

The nomenclature of oxides has been already described (p. 109). They are divided into three classes, namely, alkaline or basic oxides, neutral oxides, and oxides possessing acid characters. In practice the term oxide is usually restricted to bodies belonging to the first two groups, those of the third being simply called acids. Generally speaking, these acids are derived from the non-metallic elements, which yield no basic oxides; many of the metals, however, yield acids of a more or less energetic description.

The same element in combining with oxygen in more than one proportion may yield more than one acid; in this case it has been usual to apply to the acid containing most oxygen the termination *ic*, and to the one containing the lesser quantity the termination *ous*. When more members of the same group came to be known, recourse was had to a prefix, *hypo* or *hyper*, (or *per*,) signifying deficiency or excess. Thus, the two earliest known acids of sulphur were named respectively *sulphurous* and *sulphuric* acids; subsequently two more were discovered, the one containing less oxygen than sulphurous acid, the other intermediate in composition between sulphurous and sulphuric acids. These were called *hyposulphurous* and *hyposulphuric* acids. The names of the new acids of sulphur of still more recent discovery are not yet permanently fixed; Lavoisier's system, even in its extended form, fails to furnish names for such a lengthened series. Other examples of the nomenclature of acids with increasing proportions of oxygen are easily found; as *hypophosphorous*, *phosphorous* and *phosphoric* acids; *hypochlorous*, *chlorous*, *hypochloric*, *chloric*, and *perchloric* acids; *nitrous*, *hyponitric*, and *nitric* acids, &c.

The nomenclature of salts is derived from that of the acid they contain; if the name of the acid terminate in *ic*, that of the salt is made to end in *ate*: if in *ous*, that of the saline compounds ends in *ite*. Thus, sulphuric acid forms *sulphates* of the various bases; sulphurous acid, *sulphites*; hyposulphurous acid, *hyposulphites*; hyposulphuric acid, *hyposulphates*, &c. The rule here is very simple and obvious.,

[1] *Formerly the termination uret* was likewise frequently used.

The want of uniformity in the application of the systematic nomenclature is chiefly felt in the class of oxides not possessing acid characters, and in that of some analogous compounds. The old rule was to apply the word *protoxide* to the oxide containing least oxygen, to call the next in order *binoxide*, the third *tritoxide*, or *teroxide;* &c. But latterly this rule has been broken through, and the term protoxide given to that oxide of a series in which the basic characters are most strongly marked. Any compound containing a smaller proportion of oxygen than this is called a *suboxide*. An example is to be found in the two oxides of copper; that which was once called binoxide is now protoxide, being the most basic of the two, while the former protoxide is degraded into suboxide.

The Latin prefix *per*, or rarely *hyper*, is sometimes used to indicate the highest oxide of a series destitute of acidity, as *peroxide* of iron, chromium, manganese, lead, &c. Other Latin prefixes, as *sesqui*, *bi* or *bin*, and *quad*, applied to the name of binary compounds or salts, have reference to the constitution of these latter expressed in chemical equivalents.[1] Thus, an oxide in which the proportion of oxygen and metal are in equivalents, as 1·5 to 1, or 3 to 2, is often called a sesquioxide; if in the proportion of 2 to 1, a binoxide, &c. The same terms are applied to salts; thus we have *neutral* sulphate of potassa, *sesquisulphate* of potassa, and *bisulphate* of potassa; the first containing 1 equivalent of acid to 1 of base, the second 1·5 of acid to 1 of base, and the third 2 equivalents of acid to 1 equivalent of base. In like manner we have *neutral* oxalate, *binoxalate*, and *quadroxalate* of potassa, the latter having 4 eq. of acid to 1 eq. of base. Many other cases might be cited.

The student will soon discover that the rules of nomenclature are often loosely applied, as when a Latin numeral prefix is substituted for one of Greek origin. We speak of *tersulphide* instead of tritosulphide of antimony. These and other small irregularities are not found in practice to cause serious confusion.

THE LAWS OF COMBINATION BY WEIGHT.

The great general laws which regulate all chemical combinations admit of being laid down in a manner at once simple and concise. They are four in number, and to the following effect:—

1. All chemical compounds are definite in their nature, the ratio of the elements being constant.
2. When any body is capable of uniting with a second in several proportions, these proportions bear a simple relation to each other.
3. If a body, A, unite with other bodies, B, C, D, the quantities of B, C, D, which unite with A, represent the *relations in which they unite among themselves*, in the event of union taking place.
4. The combining quantity of a compound is the sum of the combining quantities of its components.

(1.) *Constancy of Composition.*—That the same chemical compound invariably contains the same elements united in unvarying proportions, is a proposition almost axiomatic; it is involved in the very idea of identity itself. The converse, however, is very far from being true; the same elements combining in the same proportions do not of necessity generate the same substance.

Organic chemistry furnishes numerous instances of this very remarkable fact, in which the greatest diversity of properties is associated with identity of chemical composition. These cases seem to be nearly confined to organic

[1] See a few pages forward.

mistry; only a few well-established and undoubted examples being known he organic or mineral division of the science.

2.) *Multiple Proportions.*—Illustrations of this simple and beautiful law und on every side; let the reader take for example the compounds of ogen and oxygen, five in number, containing the proportions of the two nents so described that the quantity of one of them shall remain con- it:—

	Nitrogen.	Oxygen.
Protoxide	14	8
Binoxide	14	16
Nitrous acid	14	24
Hyponitric acid	14	32
Nitric acid	14	40

t will be seen at a glance, that while the nitrogen remains the same, the ntities of oxygen increase by *multiples* of 8, or the number representing quantity of that substance in the first compound: thus 8, 8×2, 8×3, 4, and 8×5, give respectively the oxygen in the protoxide, the binoxide, ous acid, hyponitric acid, and lastly, nitric acid. Again, carbonic acid tains exactly twice as much oxygen in proportion to the other constituent carbonic oxide; the binoxide of hydrogen is twice as rich in oxygen as er; the corresponding sulphides exhibit the same phenomena, while the allic compounds offer one continued series of illustrations of the law, ough the ratio is not always so simple as that of 1 to 2.

t often happens that one or more members of a series are yet deficient: oxides of chlorine afford an example

	Chlorine.	Oxygen.
Hypochlorous acid	35·5	8
Chlorous acid	35·5	24
Hypochloric acid	35·5	32
Chloric acid	35·5	40
Perchloric acid	35·5	56

[ere the quantities of oxygen progress in the following order:—8, 8×3, 4, 8×5, 8×7; a gap is manifest between the first and second substances; remains to be filled up by future researches. The existence of a simple tion among the numbers in the second column is however not the less lent. Even when difficulties seem to occur in applying this principle, y are only apparent, and vanish when closely examined. In the highly plex sulphur series, given at p. 132, the numbers placed in each column multiples of the lowest amongst them; and, by making the assumption, ch is not at all extravagant, that certain of the last-named bodies are in- nediate combinations, we may arrange the four direct compounds in such anner that the sulphur shall remain a constant quantity.

	Sulphur.	Oxygen.
Hyposulphurous acid	32	16
Sulphurous acid	32	32
Hyposulphuric acid	32	40
Sulphuric acid	32	48

ompound bodies of all kinds are also subject to the law of multiples n they unite among themselves, or with elementary substances. There two sulphates of potassa and soda: the second contains twice as much l in relation to the alkaline base as the first. There are three oxalates otassa, namely, *the simple oxalate*, the binoxalate, and the quadroxalate;

the second has equally twice as much acid as the first; and the third twice as much as the second. Many other cases might be cited, but the student, once in possession of the principle, will easily notice them as he proceeds.

(8.) *Law of Equivalents.* — It is highly important that the subject now to be discussed should be completely understood.

Let a substance be chosen whose range of affinity and powers of combination are very great, and whose compounds are susceptible of rigid and exact analysis; such a body is found in oxygen, which is known to unite with all the elementary substances, with the single exception of fluorine. Now, let a series of exact experiments be made to determine the proportions in which the different elements combine with one and the same constant quantity of oxygen, which, for reasons hereafter to be explained, may be assumed to be 8 parts by weight; and let these numbers be arranged in a column opposite the names of the substances. The result is a table or list like the following, but of course much more extensive when complete.

Oxygen	8
Hydrogen	1
Nitrogen	14
Carbon	6
Sulphur	16
Phosphorus	32
Chlorine	35·5
Iodine	127
Potassium	39
Iron	28
Copper	31·7
Lead	103·7
Silver	108
&c. &c.	

Now the law in question is to this effect: — If such numbers represent the proportions in which the different elements combine with the arbitrarily-fixed quantity of the starting substance, the oxygen, they also represent the *proportions in which they unite among themselves*, or at any rate bear some exceedingly simple ratio to these proportions.

Thus, hydrogen and chlorine combine invariably in the proportions 1 and 35·5; hydrogen and sulphur, 1 to 16; chlorine and silver, 35·5 to 108; iodine and potassium, 127 parts of the former to 39 of the latter, &c. This rule is never departed from in any one instance.

The term *equivalent* is applied to these numbers for a reason which will now be perfectly intelligible; they represent quantities capable of exactly replacing each other in combination: 1 part of hydrogen goes as far in combining with or saturating a certain amount of oxygen as 28 parts of iron, 39 of potassium, or 108 of silver; for the same reasons, the numbers are said to represent *combining quantities*, or *proportionals*.

Nothing is more common than to speak of so many equivalents of this or that substance being united to one or more equivalents of a second; by this expression, quantities are meant just so many times greater than these relative numbers. Thus, sulphuric acid is said to contain 1 equivalent of sulphur and 3 equivalents of oxygen; that is, a quantity of the latter represented by three times the combining number of oxygen; phosphoric acid is made up of 1 equivalent of phosphorus and 5 of oxygen; the red oxide of iron contains, as will be seen hereafter, 3 equivalents of oxygen to every 2 equivalents of metal, &c. It is an expression which will henceforward be

nd constantly employed; it is hoped, therefore, that it will be under-

ıature of the law will easily show that the choice of the body destined for a point of departure is perfectly arbitrary, and regulated by con- ›ns of convenience alone.

ly might be chosen which refuses to unite with a considerable num- he elements, and yet the equivalents of the latter would admit of ›termined by indirect means, in virtue of the very peculiar law under on. Oxygen does not unite with fluorine, yet the equivalent of the ın be found by observing the quantity which combines with the *equi-* uantity of hydrogen or calcium, already known. We may rest as- ıat if an oxide of fluorine be ever discovered, its elements will be ed in the ratio of 8 to 19, or in numbers which are either multiples ultiples of these.

umber assigned to the starting-substance is also equally arbitrary; table given, oxygen instead of 8 were made 10, or 100, or even a l number, it is quite obvious that although the other numbers would fferent, the *ratio*, or proportion among the whole, would remain un- , and the law would still be maintained in all its integrity.

are in fact two such tables in use among chemists; one in which is made = 8, and a second in which it is made = 100; the former ally used in this country and England, and the latter still to a extent on the Continent. The only reason for giving, as in the pre- ume, a preference to the first is, that the numbers are smaller and sily remembered.

umber 8 has been chosen in this table to represent oxygen, from an long held by the late Dr. Prout, and recently to appearance substan- some remarkable instances by very elaborate investigation, that the nts of all bodies are multiplies of that of hydrogen; and, conse- by making the latter unity, the numbers would be all integers. The must be considered as altogether unsettled. A great obstacle to iew is presented by the case of chlorine, which certainly seems to be ınal number; and one single well-established exception will be fatal ypothesis.

experimental investigations are attended with a certain amount of he results contained in the following table must be looked upon ıs good approximations to the truth. For the same reason, small ›es are often observed in the determination of the equivalents of the dies by different experimenters.

TABLE OF ELEMENTARY SUBSTANCES, WITH THEIR EQUIVALENTS.

	Oxy. = 8.	Oxy. = 100.		Oxy. = 8.	Oxy. = 100.
Aluminium	13·7	171·25	Nickel	29·6	370
Antimony	129	1612·5	Niobium		
Arsenic	75	937·5	Nitrogen	14	175
Barium	68·5	856·25	Norium		
Beryllium	6·9	86·25	Osmium	99·6	1245
Bismuth	213	2662·5	Oxygen	8	100
Boron	10·9	136·25	Palladium	53·3	666·25
Bromine	80	1000	Pelopium		
Cadmium	56	700	Phosphorus	32	400
Calcium	20	250	Platinum	98·7	1233·75
Carbon	6	75	Potassium	39	487·5
Cerium	47 (?)	587·5	Rhodium	52·2	652·5
Chlorine	35·5	443·75	Ruthenium	52·2	652·5
Chromium	26·7	333·75	Selenium	39·5	493·75
Cobalt	29·5	368·75	Silicium	21·3	266·25
Copper	31·7	396·25	Silver	108	1350
Didymium	50 (?)	625	Sodium	23	287·5
Erbium			Strontium	43·8	547·5
Fluorine	19	237.5	Sulphur	16	200
Gold	197	2462·5	Tantalum	184	2300
Hydrogen	1	12·5	Tellurium	64·2	802·5
Iodine	127	1587·5	Terbium		
Iridium	99	1237·5	Thorium	59·6	745
Iron	28	350	Tin	58	725
Lanthanum	47 (?)	587·5	Titanium	25	312·5
Lead	103·7	1296·25	Tungsten	92	1150
Lithium	6·5	81·25	Uranium	60	750
Magnesium	12	150	Vanadium	68·6	857·5
Manganese	27·6	345	Yttrium		
Mercury	100	1250	Zinc	32·6	407·5
Molybdenum	46	575	Zirconium	33·6	420

(4.) *Combining Numbers of Compounds.*—The law states that the equivalent or combining number of a compound is always the sum of the equivalents of its components. This is also a great fundamental truth, which it is necessary to place in a clear and conspicuous light. It is a separate and independent law, established by direct experimental evidence, and not deducible from either of the preceding.

The method of investigation by which the equivalent of a simple body is determined, has been already explained; that employed in the case of a compound is in nowise different. The example of the acids and alkalis may be taken as the most explicit, and at the same time most important. An acid and a base, combined in certain definite proportions, *neutralize*, or mask each other's properties completely, and the result is a salt; these proportions are called the equivalents of the bodies, and they are very variable. Some acids have very high capacities of saturation, of others a much larger quantity must be employed to neutralize the same amount of base; the bases themselves present also similar phenomena. Thus, to saturate 47 parts of potassa, or 116 parts of oxide of silver, there are required

40	parts	sulphuric acid,
54	"	nitric acid,
75·5	"	chloric acid,
167	"	iodic acid,
51	"	acetic acid.

mbers very different, but representing quantities which replace each in combination. Now, if a quantity of some base, such as potassa, be , which is represented by the sum of the equivalents of potassium and en, then the quantity of any acid requisite for its neutralization, as deined by direct experiment, will always be found equal to the sum of the alents of the different components of the acid itself.

39=equivalent of potassium.
8= " oxygen.
—
47=assumed equivalent of potassa.

parts of potassa are found to be exactly neutralized by 40 parts of real hurio acid, or by 54 parts of real nitric acid. These quantities are ntly made up by adding together the equivalents of their constituents:—

equivalent of sulphur = 16	1 equivalent of nitrogen = 14
" oxygen = 24	5 " oxygen = 40
—	—
" sulphuric acid = 40	1 " nitric acid = 54

d the same is true if any acid be taken, and the quantities of different required for its neutralization determined; the combining number e compound will always be found to be the sum of the combining num- of its components, however complex the substance may be. Even g such bodies as the vegeto-alkalis of organic chemistry, the same uni- l rule holds good. When salts combine, which is a thing of very com- occurrence, as will hereafter be seen, it is always in the ratio of the alent numbers. Apart from hypothetical consideration, no *à priori* m can be shown why such should be the case; it is, as before remarked, dependent law, established like the rest, by experiment.

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curious observation was very early made to this effect:—If two neutra which decompose each other when mixed, be brought in contact, the ompounds resulting from their mutual decomposition will also be neutral. example, when solution of nitrate baryta and sulphate of potassa are led, they both suffer decomposition, sulphate of baryta and nitrate of sa being simultaneously formed, both of which are perfectly neutral. reason of this will be at once evident; interchange of elements can take place by the displacement of equivalent quantities of matter on r side. For every 54 parts of nitric acid set free by the decomposition e barytic salt, 47 parts of potassa are abandoned by the 40 parts of uric acid with which they were previously in combination, now trans- d to the baryta. But 54 and 47 are the representatives of combining tities; hence the new compound must be neutral.

COMBINATION BY VOLUME.

any years ago, M. Gay-Lussac made the very important and interesting very that when gases combine chemically, union invariably takes place r between equal volumes, or between volumes which bear a simple rela- to each other. *This is not only* true of elementary gases, but of com-

pound bodies of this description, as it is invariably observed that the contraction of bulk which so frequently follows combination itself also bears a simple relation to the volumes of the combining gases. The consequence of this is, that compound gases and the vapours of complex volatile liquids (which are truly gases to all intents and purposes) follow the same law as elementary bodies, when they unite with these latter or combine among themselves.

The ultimate reason of the law in question is to be found in the very remarkable relation established by the hand of Nature between the specific gravity of a body in the gaseous state and its chemical equivalent;— a relation of such a kind that quantities by weight of the various gases expressed by their equivalents, or in other words, quantities by weight which combine, occupy under similar circumstances of pressure and temperature either equal volumes, or volumes bearing a similar proportion to each other. In the example cited below, equivalent weights of hydrogen, chlorine, and iodine-vapour, occupy equal volumes, while the equivalent of oxygen occupies exactly half that measure.

	Cubic inches.
8·0 grains of oxygen occupy at 60° (15°·5C) and 30 inches barom.	23·3
1·0 grain of hydrogen	46·7
35·5 grains of chlorine	46·2
127·0 grains of iodine-vapour (would measure)	46·7

If both the specific gravity and the chemical equivalent of a gas be known, its equivalent or combining volume can be easily determined, since it will be represented by the number of times the weight of an unit of volume (the specific gravity) is contained in the weight of one chemical equivalent of the substance. In other words, the equivalent volume is found by dividing the chemical equivalent by the specific gravity. The following table exhibits the relations of specific gravity, equivalent weight, and equivalent volume of the principal elementary substances.

	Sp. gravity.	Equiv. weight.	Equiv. volume.
Hydrogen	0·0693	1·0	14·43 or 1
Nitrogen	0·972	14·0	14·37 " 1
Chlorine	2·470	35·5	14·33 " 1
Bromine-vopour	5·395	80·0	14·82 " 1
Iodine-vapour	8·716	127·0	14·57 " 1
Carbon-vapour[1]	0·418	6·0	14·34 " 1
Mercury-vapour	7·000	100·0	14·29 " 1
Oxygen	1·106	8·0	7·23 " ½
Phosphorus-vapour	4·350	32·0	7·35 " ½
Arsenic-vapour	10·420	75·0	7·19 " ½
Sulphur-vapour	6·654	16·0	2·40 " ⅙

Thus it appears that hydrogen, nitrogen, chlorine, bromine, iodine, carbon, and mercury, in the gaseous state, have the same equivalent volume; oxygen, phosphorus, and arsenic, one-half of this; and sulphur one-sixth. The slight discrepancies in the numbers in the third column result chiefly from errors in the determination of the specific gravities.

Compound bodies exhibit exactly similar results:—

[1] See farther on.

	Sp. gravity.	Equiv. weight.	Equiv. volume.
ater-vapour	0·625	9·0	14·40 or 1
otoxide of nitrogen	1·525	22·0	14·43 " 1
lphuretted hydrogen	1·171	17·0	14·51 " 1
lphurous acid	2·210	32·0	14·52 " 1
rbonic oxide	0·973	14·0	14·39 " 1
rbonic acid	1·524	22·0	14·43 " 1
ght carbonetted hydrogen	0·559	8·0	14·31 " 1
efiant gas	0·981	14·0	14·27 " 1
noxide of nitrogen	1·039	30·0	28·87 " 2
ydrochloric acid	1·269	36·5	28·70 " 2
osphoretted hydrogen	1·240	35·0	28·22 " 2
nmonia	0·589	17·0	28·86 " 2
her-vapour	2·586	37·0	14·31 " 1
etone-vapour	2·022	29·0	14·34 " 1
nzol-vapour	2·738	78·0	28·49 " 2
cohol-vapour	1·613	46·0	28·52 " 2

In the preceding tables the ordinary standard of specific gravity for gases, mospheric air, has been taken. It is, however, a matter of perfect indifrence what substance be chosen for this purpose: the numbers representg the combining volumes will change with the divisor, but the proportions ey bear to each other will remain unaltered. And the same remark plies to the equivalent weights; either of the scales in use may be taken, ovided that it be adhered to throughout.

The law of volumes often serves in practice to check and corroborate the sults of experimental investigation, and is often of great service in this spect.

There is an expression sometimes made use of in chemical writings which is necessary to explain, namely, the meaning of the words *hypothetical deny of vapour*, applied to a substance which has never been volatilized, such carbon, whose real specific gravity in that state must of course be unown; it is easy to understand the origin of this term. Carbonic acid conins a volume of oxygen equal to its own; consequently, if the specific avity of the latter be subtracted from that of the former gas, the residue ill express the proportion borne by the weight of the carbon, certainly en in a vaporous state, to that of the two gases.

The specific gravity of carbonic acid is	1·5240
That of oxygen is	1·1057
	0·4183

On the supposition that carbonic acid contains equal volumes of oxygen nd this vapour of carbon, condensed to one-half, the latter will have the ecific gravity represented by 0·4183 and the combining volume given in the ble. But this is merely a supposition, a guess; no proof can be given at carbonic acid gas is so constituted. All that can be safely said is conined in the prediction, that, should the specific gravity of the vapour of rbon ever be determined, it will be found to coincide with this number, or bear some simple and obvious relation to it.

For many years past, attempts have been made to extend to solids and quids the results of Gay-Lussac's discovery of the law of gaseous combiation by volume, the combining or equivalent volumes of the bodies in uestion being determined by the method pursued in the case of gases, amely, by dividing the chemical equivalent by the specific gravity. The

By such a system, the eye is enabled to embrace the whole at a glance, and gain a distinct idea of the composition of the body, and its relations to others similarly described.

Some authors are in the habit of making use of contractions, which, however, are by no means generally adopted. Thus, two equivalents of a substance are indicated by the symbol with a short line drawn through or below it; an equivalent of oxygen is signified by a dot, and one of sulphur by a comma. These alterations are sometimes convenient for abbreviating a long formula, but easily liable to mistakes. Thus,

Sesquioxide of iron $\underline{Fe}O^3$, or $\not{F}eO^3$, or Fe, instead of Fe_2O_3

Bisulphide of carbon $\ddot{\breve{C}}$, instead of CS_2

Crystallized alum as before $\underline{\bar{Al}}\,\bar{S}_3 + \dot{K}\bar{S} + 24H$.

THE ATOMIC THEORY.

That no attempt should have been made to explain the reason of the very remarkable manner in which combination occurs in the production of chemical compounds, and to point out the nature of the relations between the different modifications of matter which fix and determine these peculiar and definite changes, would have been unlikely, and in contradiction with the speculative tendency of the human mind. Such an attempt, and a very ingenious and successful one it is, has been made, namely, the atomic hypothesis of Dr. Dalton.

From very ancient times, the question of the constitution of matter with respect to divisibility has been debated, some adopting the opinion that this divisibility is infinite, and others, that when the particles become reduced to a certain degree of tenuity, far indeed beyond any state that can be reached by mechanical means, they cease to be farther diminished in magnitude; they become, in short, *atoms*.[1] Now, however the imagination may succeed in figuring to itself the condition of matter on either view, it is hardly necessary to mention that we have absolutely no means at our disposal for deciding such a question, which remains at the present day in the same state as when it first engaged the attention of the Greek philosophers, or perhaps that of the sages of Egypt and Hindostan long before them.

Dr. Dalton's hypothesis sets out by assuming the existence of such atoms or indivisible particles, and states, that compounds are formed by the union of atoms of different bodies, one to one, one to two, &c. The compound atom joins itself in the same manner to a compound atom of another kind, and a combination of the second order results. Let it be granted, farther, that the relative weights of the atoms are in the proportions of the equivalent numbers, and the hypothesis becomes capable of rendering consistent and satisfactory reasons for all the consequences of those beautiful laws of combination lately discussed.

Chemical compounds must always be definite; they must always contain the same number of atoms, of the same kind, arranged in a similar manner. The same kind and number of atoms need not, however, of necessity produce the same substance, for they may be differently arranged; and much depends upon this circumstance.

Again, the law of multiple proportions is perfectly well explained; an atom

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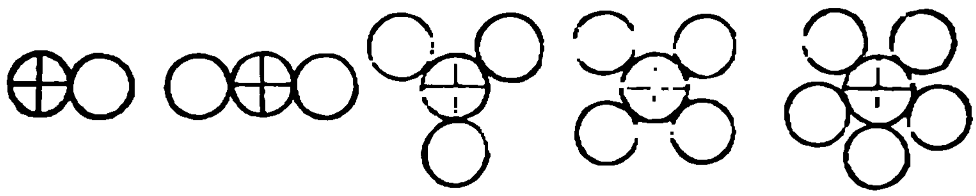
[1] Ἄτομος, that which cannot be cut.

trogen unites with one of oxygen to form laughing gas: with two, to binoxide of nitrogen; with three, to produce nitrous acid; with four, nitric acid; and with five, nitric acid.—perhaps something after the ier represented in fig. 124, in which the circle with a cross represents tom of nitrogen, and the plain circle that of oxygen.

Fig. 124.

Protoxide. Binoxide. Nitrous acid. Hyponitric acid. Nitric acid.



ro atoms of one substance may unite themselves with three or even with i of another, as in the case of one of the acids of manganese; but such inations are rare.

e mode in which bodies replace, or may be substituted for, each other, o perfectly intelligible, as a little consideration will show.

nally, the law which fixes the equivalent of a compound at the sum of equivalents of the components, receives an equally satisfactory explan.

e difficulties in the general application of the atomic hypothesis are ly felt in attempting to establish some wide and universal relation ben combining number and combining volume, among gases and vapours, n the case of the highly complex products of organic chemistry. These oles have grown up in comparatively recent times. On the other hand, emarkable observations of the specific capacities for heat of equivalent tities of the solid elementary substances, might be urged in favour of or some similar molecular hypothesis. But even here serious discreps exist; we may not take liberties with equivalent numbers determined xact chemical research, and, in addition, a simple relation is generally l to be wanting between the capacity for heat of the compound and that i elements.

e theory in question has rendered great service to chemical science: it xcited a vast amount of inquiry and investigation, which have contribuery largely to define and fix the laws of combination themselves. In recent days it is not impossible, that, without some such hypothetical , the exquisitely beautiful relations which Mitscherlich and others have n to exist between crystalline form and chemical composition, might have been brought to light, or, at any rate, their discovery might been greatly delayed. At the same time, it is indispensable to draw roadest possible line of distinction between this, which is at the best graceful, ingenious, and, in its place, useful hypothesis, and those general laws of chemical action which are the pure and unmixed result luctive research.[1]

Chemical Affinity.

e term chemical affinity, or chemical attraction, has been invented to ibe that particular power or force, in virtue of which, union, often of a intimate and permanent nature, takes place between two or more

[1] e expression *atomic weight* is very often substituted for that of equivalent weight, and act, *in almost every case to be* understood as such: it is, perhaps, better avoided.

bodies, in such a way as to give rise to a *new* substance, having, for the most part, properties completely in discordance with those of its components.

The attraction thus exerted between different kinds of matter is to be distinguished from other modifications of attractive force which are exerted indiscriminately between all descriptions of substances, sometimes at enormous distances, and sometimes at intervals quite inappreciable. Examples of the latter are to be seen in cases of what is called *cohesion*, when the particles of solid bodies are immovably bound together into a mass. Then there are other effects of, if possible, a still more obscure kind; such as the various actions of surface, the adhesion of certain liquids to glass, the repulsion of others, the ascent of water in narrow tubes, and a multitude of curious phenomena which are described in works on Natural Philosophy, under the head of *molecular actions*. From all these, true chemical attraction may be at once distinguished by the deep and complete change of characters which follows its exertion: we might define affinity to be a force by which new substances are generated.

It seems to be a general law that bodies most opposed to each other in chemical properties evince the greatest tendency to enter into combination, and, conversely, bodies between which strong analogies and resemblances can be traced, manifest a much smaller amount of mutual attraction. For example, hydrogen and the metals tend very strongly indeed to combine with oxygen, chlorine, and iodine; the attraction between the different members of these two groups is incomparably more feeble. Sulphur and phosphorus stand, as it were, mid-way: they combine with substances of one and the other class, their properties separating them sufficiently from both. Acids are drawn towards alkalis, and alkalis towards acids, while union among themselves rarely, if ever, takes place.

Nevertheless, chemical combination graduates so imperceptibly into mere mechanical mixture, that it is often impossible to mark the limit. Solution is the result of a weak kind of affinity existing between the substance dissolved and the solvent; an affinity so feeble as completely to lose one of its most prominent features when in a more exalted condition, namely, power of causing elevation of temperature: for in the act of mere solution the temperature falls, the heat of combination being lost and overpowered by the effects of change of state.

The force of chemical attraction thus varies greatly with the nature of the substances between which it is exerted; it is influenced, moreover, to a very large extent by external or adventitious circumstances. An idea formerly prevailed that the relations of affinity were fixed and constant between the same substances, and great pains were taken in the preparation of tables exhibiting what was called the precedence of affinities. The order pointed out in these lists is now acknowledged to represent the order of precedence *for the circumstances* under which the experiments were made, but nothing more; so soon as these circumstances become changed, the order is disturbed. The ultimate effect, indeed, is not the result of the exercise of one single force, but rather the joint effect of a number, so complicated and so variable in intensity, that it is but seldom possible to predict the consequences of any yet untried experiment. The following may serve as examples of the tables alluded to; the first illustrates the relative affinities of a number of bases for sulphuric acid, each decomposing the combination of the acid with the base below it; thus, magnesia decomposes sulphate of ammonia; lime displaces the acid from sulphate of magnesia, &c. The salts are supposed to be dissolved in water. The second table exhibits the order of affinity for oxygen of several metals, mercury reducing a solution of silver, copper one of mercury, &c.

Sulphuric acid.		Oxygen.	
Baryta,	Lime,	Zinc.	Mercury,
Strontia,	Magnesia,	Lead.	Silver.
Potassa,	Ammonia.	Copper,	
Soda,			

[t will be proper to examine shortly some of these extraneous causes to ich allusion has been made, which modify to so great an extent the direct l original effects of the specific attractive force.

Alteration of temperature may be reckoned among these. When metallic rcury is heated nearly to its boiling point, and in that state exposed for a gthened period to the air, it absorbs oxygen, and becomes converted into ark red crystalline powder. This very same substance, when raised to till higher temperature, spontaneously separates into metallic mercury l oxygen gas. It may be said, and probably with truth, that the latter nge is greatly aided by the tendency of the metal to assume the vaporous te; but, precisely the same fact is observed with another metal, palladium, ich is not volatile at all, but which oxidates superficially at a red-heat, l again becomes reduced when the temperature rises to whiteness.

Insolubility and the power of vaporization are perhaps, beyond all other turbing causes, the most potent; they interfere in almost every reaction ich takes place, and very frequently turn the scale when the opposed forces not greatly differ in energy. It is easy to give examples. When a solu- 1 of lime in hydrochloric acid is mixed with a solution of carbonate of monia, double interchange ensues, carbonate of lime and hydrochlorate ammonia being generated. Here the action can be shown to be in a great asure determined by the insolubility of the carbonate of lime. Again, ' carbonate of lime, powdered and mixed with hydrochlorate of ammonia, l the whole heated in a retort, gives a sublimate of carbonate of ammonia, ile chloride of calcium remains behind. In this instance, it is no doubt great volatility of the ammoniacal salt which chiefly determines the kind decomposition.

When iron-filings are heated to redness in a porcelain tube, and vapour of ter passed over them, the water undergoes decomposition with the utmost ility, hydrogen is rapidly disengaged, and the iron converted into oxide. the other hand, oxide of iron heated in a tube through which a stream dry hydrogen is passed, suffers almost instantaneous reduction to the tallic state, while the vapour of water, carried forward by the current of , escapes as a jet of steam from the extremity of the tube. In these periments, the affinities between the iron and oxygen, and the hydrogen l oxygen, are so nearly balanced, that the difference of *atmosphere* is suf- ent to settle the point. An atmosphere of steam offers little resistance the escape of hydrogen; one of hydrogen bears the same relation to steam; l this apparently trifling difference of circumstances is quite enough for purpose.

The decomposition of vapour of water by white-hot platinum, pointed out Mr. Grove, will probably be referred in great part to this influence of nosphere, the steam offering great facilities for the assumption of the stic condition by the oxygen and hydrogen. The decomposition ceases soon as these gases amount to about 1-3000th of the bulk of the mixture, l can only be renewed by their withdrawal. The attraction of oxygen hydrogen is probably much weakened by the very high temperature. The ombination of the gases by the heated metal is rendered impossible by ir state of dilution.

What is called the nascent state is one very favourable to chemical com- ation. Thus *carbon and nitrogen* refuse to combine with gaseous hy-

bodies, ... simultaneously liberated from some part, ... great ease, as when organic matters ... ous putrefactive change. There is a ... the same time very extensive class of ... the general title of cases of ... affinity ... from zinc and sulphuric acid is one of ... polished zinc or iron, put into pure water, ... posing the latter to the smallest extent; it ... any length of time. On the addition, however, ... hydrogen is at once freely disengaged and the ... dissolved. Now, the only intelligible function ... the oxide as fast as it is produced; but why is ... is present, and not otherwise? The question ...

... amples of this curious indirect action might be ... does not oxidize at any temperature; nay more, ... posed by simple heat; yet if the finely-divided metal ... matter and alkali, and ignited, the whole fuses to a ... silicate of silver. Platinum is attacked by fused ... hydrogen is ... disengaged while the metal is ... effect which never happens to silver under the same circumstances ... silver is a much more oxidable substance than platinum ... potassa forms with the oxide of the last-named ... combination, in which the oxide of platinum acts as ... formation under the ... influence of the power-...

... decomposition suffered by various organic bodies when ... caustic alkali or lime, we have other examples of the ... are generated which are never formed in the absence ... is invariably less complicated, and its results fewer ... definite, than in the event of simple destruction by a ... the evaporation of light carburetted hydrogen by the new ... described, is an excellent example.

... more obscure class of phenomena, in which effects are ... mere presence of a substance, which itself undergoes ... the experiment mentioned in the article on oxygen, ... obtained, with the greatest facility, by heating a mixture ... potassa and binoxide of manganese, is an excellent case ... decomposed at a very far lower temperature than ... required. The oxide of manganese, however, is not in ... altered; it is found, after the experiment, in the same ... name *catalysis* is sometimes given to these peculiar ... the expression is not significant, and may be for that ... possible, as it suggests no explanation.

... remark, that the contact-decompositions alluded to are ... with other effects, which are, in reality, much more in-... of finely-divided platinum upon certain gaseous mixtures ... and really seems to have the power of condensing the ... extended surface, and thereby inducing combination by ... within the sphere of their mutual attractions.

ELECTRO-CHEMICAL DECOMPOSITION: CHEMISTRY OF THE VOLTAIC PILE.

When a voltaic current of considerable power is made to traverse various compound liquids, a separation of the elements of these liquids ensues: provided that the liquid be capable of conducting a current of a certain degree of energy, its decomposition almost always follows.

The elements are disengaged solely at the limiting surfaces of the liquid: where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions appearing perfectly quiescent. In addition, the elements are not separated indifferently and at random at these two surfaces, but, on the contrary, make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character, namely, oxygen, chlorine, iodine, acids, &c., at the surface connected with the *copper* or *positive* end of the battery: hydrogen, the metals, &c., at the surface in connection with the *zinc* or *negative* extremity of the arrangement.

The termination of the battery itself, usually, but by no means necessarily, of metal, are designated poles or *electrodes*,[1] as by their intervention the liquid to be experimented on is made a part of the circuit. The process of decomposition by the current is called *electrolysis*,[2] and the liquids, which, when thus treated, yield up their elements, are denominated *electrolytes*.

When a pair of platinum plates are plunged into a glass of water to which a few drops of oil of vitriol have been added, and the plates connected by wires with the extremities of an active battery, oxygen is disengaged at the positive electrode, and hydrogen at the negative, in the proportion of one measure of the former to two of the latter nearly. This experiment has before been described.[3]

A solution of hydrochloric acid mixed with a little Saxon blue (indigo), and treated in the same manner, yields hydrogen on the negative side, and chlorine on the positive, the indigo there becoming bleached.

Iodide of potassium dissolved in water is decomposed in a similar manner, and with still greater ease; the free iodine at the positive side can be recognized by its brown colour, or by the addition of a little gelatinous starch.

Every liquid is not an electrolyte; many refuse to conduct, and no decomposition can then occur; alcohol, ether, numerous essential oils, and other products of organic chemistry, besides a few saline inorganic compounds, act in this manner, and completely arrest the current of a very powerful battery. It is a very curious fact, and well deserves attention, that very nearly, if not all the substances acknowledged to be susceptible of electrolytic decomposition, belong to one class; they are all binary compounds, containing single

[1] From ἤλεκτρον, and ὁδός, a way.
[2] From ἤλεκτρον, and λύω, I loose.
[3] *Page 115.*

equivalents of their components, the latter being strongly opposed to each other in their chemical relations, and held together by very powerful affinities.

The amount of power required to effect decomposition varies greatly; solution of iodide of potassium, melted chloride of lead, solution of hydrochloric acid, water mixed with a little oil of vitriol, and pure water, demand in this respect very different degrees of electrical force, the resistance to decomposition increasing from the first-mentioned substance to the last.

One of the most important and indispensable conditions of electrolysis is fluidity: bodies which when reduced to the liquid condition freely conduct and as freely suffer decomposition, become absolute insulators to the electricity of the battery when they become solid. Chloride of lead offers a good illustration of this fact: when fused in a little porcelain crucible it gives up its elements with the utmost ease, and a galvanometer, interposed somewhere in the circuit, is strongly affected. But when the source of heat is withdrawn, and the salt suffered to solidify, all signs of decomposition cease, and at the same moment the magnetic needle reassumes its natural position. In the same manner the thinnest film of ice completely arrests the current of a powerful voltaic apparatus: the instant the ice is liquefied at any one point, so that water-communication may be restored between the electrodes, the current again passes, and decomposition occurs. Fusion by heat, and solution in aqueous liquids, answer the purpose equally well. A fluid substance may conduct a strong current of electricity without being decomposed; there are a few examples already known; the electrolysis of a solid is, from its physical properties, of course out of the question.

Liquids often exhibit the property of conduction for currents strong enough to be indicated by the galvanometer, but yet incapable of causing decomposition in the manner described. These currents may be conveyed through extensive masses of liquids; the latter seem, under these circumstances, to conduct after the manner of metals, without perceptible molecular change.

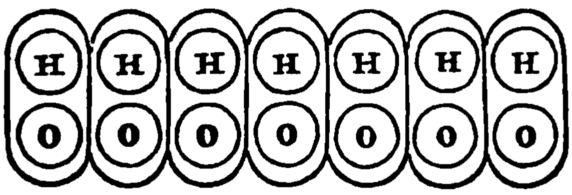
The metallic terminations of the battery, the poles or electrodes, have, in themselves, nothing in the shape of attractive or repulsive power for the elements so often separated at their surfaces. Finely-divided metal suspended in water, or chlorine held in solution in that liquid, shows not the least symptom of a tendency to accumulate around them: a single element is altogether unaffected, directly at least; severance from that previous combination is required, in order that this appearance should be exhibited.

It is necessary to examine the process of electrolysis a little more closely. When a portion of water, for example, is subjected to decomposition in a glass vessel with parallel sides, oxygen is disengaged at the positive electrode, and hydrogen at the negative; the gases are perfectly pure and unmixed. If, while the decomposition is rapidly proceeding, the intervening water be examined by a beam of light, or by other means, not the slightest disturbance or movement of any kind will be perceived, nothing like currents in the liquid or bodily transfer of gas from one part to another can be detected, and yet two portions of water, separated perhaps by an interval of four or five inches, may be respectively evolving pure oxygen and pure hydrogen.

There is, it would seem, but one mode of explaining this and all similar cases of regular electrolytic decomposition; this is by assuming that *all* the particles of water between the electrodes, and by which the current is conveyed, simultaneously suffer decomposition, the hydrogen travelling in one direction and the oxygen in the other. The neighbouring elements, thus brought into close proximity, unite and reproduce water, again destined to be decomposed by a repetition of the same change. In this manner each particle of hydrogen may be made to travel in one direction, by becoming successively united to each particle of oxygen between itself and the negative electrode; when it reaches the latter, finding no disengaged particle of oxygen

for its reception, it is rejected as it were from the series, and thrown off in a separate state. The same thing happens to each particle of oxygen, which at the same time passes continually in the opposite direction, by combining successively with each particle of hydrogen that moment separated, with which it meets, until at length it arrives at the positive plate or wire, and is disengaged. A succession of particles of hydrogen are thus continually thrown off from the decomposing mass at one extremity, and a corresponding succession of particles of oxygen at the other. The power of the current is exerted with equal energy in every part of the liquid conductor, although its *effects* only become manifest at the very extremities. The action is one of a

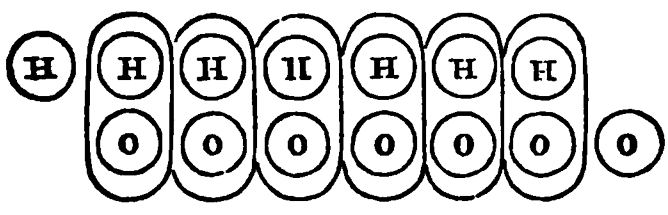
Fig. 125.



Water in usual state.

purely molecular or internal nature, and the metal terminations of the battery merely serve the purpose of completing the connection between the latter and the liquid to be decomposed. The figures 125 and 126 are intended to assist the imagination of the reader, who must at the same time avoid regarding them in any other light than that of a somewhat figurative mode of representing the curious phenomena described. The circles are intended to indicate the elements, and are distinguished by their respective symbols.

Fig. 126.



Water undergoing electrolysis.

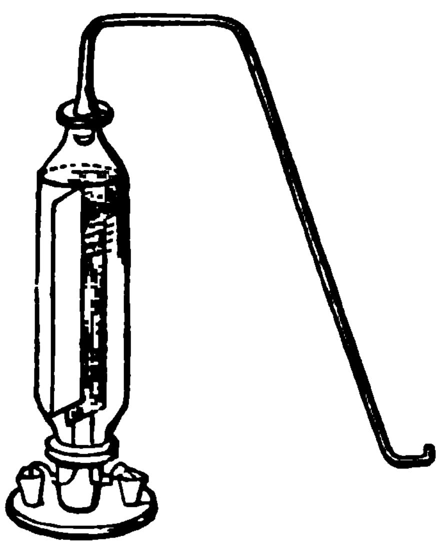
A distinction is to be carefully drawn between true and regular electrolysis, and what is called secondary decomposition, brought about by the reaction of the bodies so eliminated upon the surrounding fluid, or upon the substance of the electrodes; hence the advantage of platinum for the latter purpose when electrolytic actions are to be studied in their greatest simplicity, that metal being scarcely attacked by any ordinary agents. When, for example, a solution of nitrate or acetate of lead is decomposed by the current between platinum plates, metallic lead is deposited at the negative side, and a brown powder, binoxide of lead, at the positive: the latter substance is the result of a secondary action; it proceeds, in fact, from the nascent oxygen at the moment of its liberation reacting upon the protoxide of lead present in the salt, and converting it into binoxide, which is insoluble in the dilute acid. There is every reason to believe that when sulphuric and nitric acids seem to be decomposed by the current, the effect is really due to the water they contain becoming decomposed, and reacting by its hydrogen upon the acid; for these bodies do not belong to the class of electrolytes, as already specified, and would probably refuse to conduct could they be examined in an anhydrous condition.

If a number of different electrolytes, such as acidulated water, sulphate of copper, *iodide of potassium, fused* chloride of lead, &c., be arranged in a

series, and the same current be made to traverse the whole, all will suffer decomposition at the same time, but by no means to the same amount. If arrangements be made by which the quantities of the eliminated elements can be accurately ascertained, it will be found, when the decomposition has proceeded to some extent, that these latter will have been disengaged exactly in the *ratio of the chemical equivalents.* The same current which decomposes 9 parts of water will separate into their elements 166 parts of iodide of potassium, 139·2 parts of chloride of lead, &c. Hence the very important conclusion: The action of the current is perfectly definite in its nature, producing a fixed and constant amount of decomposition, expressed in each electrolyte by the value of its chemical equivalent.

From a very extended series of experiments, based on this and other methods of research, Mr. Faraday was enabled to draw the general inference that effects of chemical decomposition were always proportionate to the quantity of circulating electricity, and might be taken as an accurate and trustworthy measure of the latter. Guided by this highly important principle, he constructed his *voltameter*, an instrument which has rendered the greatest service to electrical science. This is merely an arrangement by which a little acidulated water is decomposed by the current, the gas evolved being collected and measured. By placing such an instrument in any part of the circuit, the quantity of electric force necessary to produce any given effect can be at once estimated; or, on the other hand, any required amount of the latter can be, as it were, measured out and adjusted to the object in view. The voltameter has received many different forms; one of the most extensively useful is that shown in fig. 127, in which the platinum plates are separated by a very small interval, and the gas is collected in a graduated jar standing on the shelf of the pneumatic trough, the tube of the instrument, which is filled to the neck with dilute sulphuric acid, being passed beneath the jar.

Fig. 127.



The decompositions of the voltaic battery can be effected by the electricity of the common machine, by that developed by magnetic action, and by that of animal origin, but to an extent incomparably more minute. This arises from the very small *quantity* of electricity set in motion by the machine, although its *tension*, that is, power of overcoming obstacles, and passing through imperfect conductors, is exceedingly great. A pair of small wires of zinc and platinum, dipping into a single drop of dilute acid, develope far more electricity, to judge from the chemical effects of such an arrangement, than very many turns of a large plate electrical machine in high action. Nevertheless, polar or electrolytic decomposition can be distinctly and satisfactorily effected by the latter, although on a minute scale.

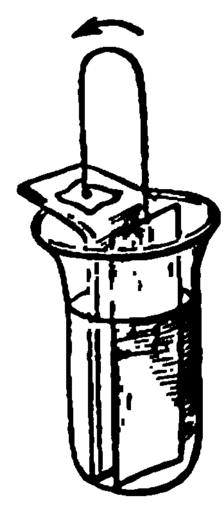
With a knowledge of the principles laid down, the study of the voltaic battery may be resumed and completed. In the first place, two very different views have been held concerning the source of the electrical disturbance in that apparatus. Volta himself ascribed it to mere contact of dissimilar metals; to what was denominated an *electro-motive* force, called into being by such contact; the liquid merely serving the purpose of a conductor between one pair of metals and that succeeding. Proof was supposed to be given of the fundamental position by an experiment in which discs of zinc and copper attached to insulating handles, after being brought into close contact, were found, by the aid of a very delicate gold-leaf electroscope, to be in opposite electrical states. It appears, however, that the more carefully

is experiment is made, the smaller is the effect observed; and hence it is dged highly probable that the whole may be due to accidental causes, ainst which it is almost impossible to guard.

On the other hand, the observation was soon made that the power of the ttery always bore some kind of proportion to the chemical action upon the ic; that, for instance, when pure water was used the effect was extremely ble; with a solution of salt, it became much greater; and, lastly, with lute acid, greatest of all; so that some relation evidently existed between e chemical effect upon the metal, and the evolution of electrical force.

The experiments of Mr. Faraday and Professor Daniell have given very eat support to the chemical theory, by showing that contact of dissimilar etals is *not* necessary in order to call into being powerful electrical currents, d that the development of electrical force is not only in me way connected with the chemical action of the liquid of e battery, but that it is always in direct proportion to the tter. One very beautiful experiment, in which decompo- tion of iodide of potassium by real electrolysis is performed r a current generated without any contact of dissimilar etals, can be thus made:—A plate of zinc (fig. 128) is nt at a right angle, and cleaned by rubbing with sand- per. A plate of platinum has a wire of the same metal tached to it by careful rivetting, and the latter bent into arch. A piece of folded filter-paper is wetted with a so- tion of iodide of potassium, and placed upon the zinc; the atinum plate is arranged opposite to the latter, with the d of its wire resting upon the paper, and then the pair unged into a glass of dilute sulphuric acid, mixed with a w drops of nitric. A brown spot of iodine becomes in a moment evident neath the extremity of the platinum wire; that is, at the positive side of e arrangement.

Fig. 128.



A strong argument in favour of the chemical view is founded on the easily- oved fact, that the direction of the current is determined by the kind of tion upon the metals, the one least attacked being always positive. Let o polished plates, the one iron and the other copper, be connected by wires ith a galvanometer, and then immersed in a solution of an alkaline sul- hide. The needle in a moment indicates a powerful current, passing from e copper, through the liquid, to the iron, and back again through the wire. et the plates be now removed, cleaned, and plunged into dilute acid; the edle is again driven round, but in the opposite direction, the current now ssing from the iron, through the liquid, to the copper. In the first instance e copper is acted upon, and not the iron; in the second, these conditions e reversed, and with them the direction of the current.

The metals employed in the practical construction of voltaic batteries are nc for the active metal, and copper, silver, or, still better, platinum for the active one; the greater the difference of oxidability, the better the arrange- ent. The liquid is either dilute sulphuric acid, sometimes mixed with a ttle nitric, or occasionally, where very slow and long-continued action is anted, salt and water. To obtain the maximum effect of the apparatus ith the least expenditure of zinc, that metal must be employed in a pure ate, or its surface must be covered by or amalgamated with mercury, which its electrical relations closely resembles the pure metal. The zinc is easily ought into this condition by wetting it with dilute sulphuric acid, and then bbing a little mercury over it by means of a piece of rag tied to a stick.

The principle of the compound battery is, perhaps, best seen in the crown cups; by each alternation of zinc, fluid, and copper, the current is urged wards with increased energy, its intensity is augmented, but the actual

...ount of electrical force thrown into the current form is not increased. ...e quantity, estimated by its decomposing power, is, in fact, determined ... that of the smallest and least active pair of plates, the quantity of elec...ricity in every part or section of the circuit being exactly equal. Hence ...arge and small plates, batteries strongly and weakly charged, can never be ...connected without great loss of power.

When a battery, either simple or compound, constructed with pure or with amalgamated zinc, is charged with dilute sulphuric acid, a number of highly interesting phenomena may be observed. While the circuit remains broken the zinc is perfectly inactive, no water is decomposed, no hydrogen liberated; but the moment the connection is completed, torrents of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone, while the zinc undergoes tranquil and imperceptible oxidation and solution. Thus, exactly the same effects are seen to occur in every active cell of a closed circuit, which are witnessed in a portion of water undergoing electrolysis; the oxygen appears at the positive side, with respect to the current, and the hydrogen at the negative; but with this difference, that the oxygen, instead of being set free, combines with the zinc. It is, in fact, a real case of electrolysis, and electrolytes alone are available as exciting liquids.

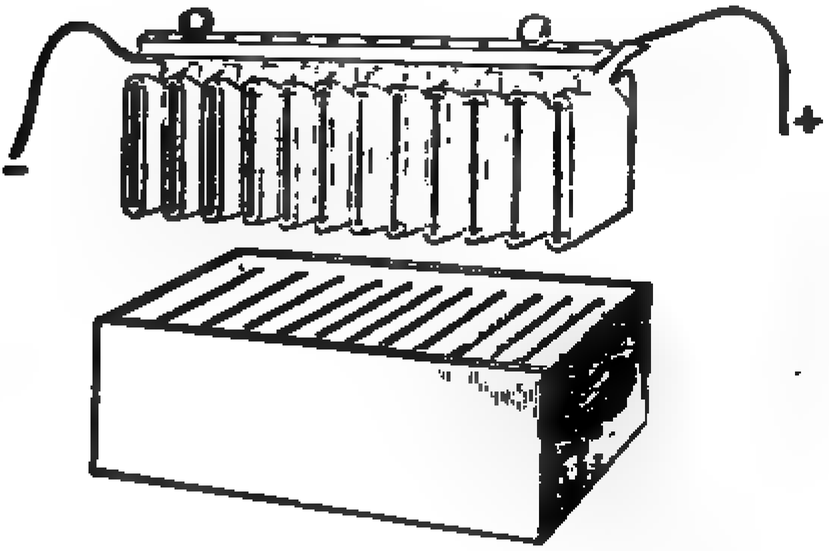
Common zinc is very readily attacked and dissolved by dilute sulphuric acid; and this is usually supposed to arise from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals or plumbago, partially embedded in the zinc. This gives rise in the battery to what is called local action, by which in the common forms of apparatus three-fourths or more of the metal are often consumed, without contributing in the least to the general effect, but, on the contrary, injuring the latter to some extent. This evil is got rid of by amalgamating the surface.

From experiments very carefully made with a "dissected" battery of peculiar construction, in which local action was completely avoided, it has been distinctly proved that the quantity of electricity set in motion by the battery varies exactly with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen, that when a perfect battery of this kind is employed to decompose water, in order to evolve 1 ...rain of hydrogen from the latter, 33 grains of zinc must be oxidized and its ...uivalent quantity of hydrogen disengaged in each active cell of the battery. That is to say, that the electrical force generated by the oxidation of an ...uivalent of zinc *in* the battery, is capable of effecting the decomposition ... an equivalent of water, or any other electrolyte *out* of it.

This is an exceedingly important discovery; it serves to show in the most ...king manner, the intimate nature of the connection between chemical and ...trical forces, and their remarkable quantitative or equivalent relations. ...lmost seems, to use an expression of Mr. Faraday, as if a transfer of ...mical force took place through the substance of solid metallic conductors; ... chemical actions, called into play in one portion of the circuit, could be ... at pleasure to exhibit their effects without loss or diminution in any ... There is an hypothesis, not of recent date, long countenanced and ...ted by the illustrious Berzelius, which refers all chemical phenomena ...lectrical forces; which supposes that bodies combine because they are in ...te electrical states; even the heat and light accompanying chemica... ... may be, to a certain extent, accounted for in this manner. In short ... such a position, that either may be assumed as cause or effect; i... ... that electricity is merely a form or modification of ordinary chemica... ..., on the other hand, that all chemical action is a manifestatio... ... force.

... useful forms of the common voltaic battery is that con... ... Wollaston (fig. 129). The copper is made completely to encircl...

Fig. 129.



se plate, except at the edges, the two metals being kept apart by pieces k or wood. Each zinc is soldered to the preceding copper, and the screwed to a bar of dry mahogany, so that the plates can be lifted r out of the acid, which is contained in an earthenware trough, divided parate cells. The liquid consists of a mixture of 100 parts water, $2\frac{1}{2}$ oil of vitriol, and 2 parts commercial nitric acid, all by measure. A r of such batteries are easily connected together by straps of sheet r, and admit of being put into action with great ease.

great objection to this and to all the older forms of the voltaic battery t the power rapidly decreases, so that after a short time scarcely the part of the original action remains. This loss of power depends partly gradual change of the sulphuric acid into sulphate of zinc, but still on the coating of hydrogen, and at a later stage, on the precipitation tallic zinc on the copper plates. It is self-evident the copper plate in the fluid became covered zinc, it would electrically, act like a zinc plate. precisely the action of the hydrogen, whereby ease of electrical power is produced. This effect, sed by the substances separated from the liquid, monly called polarization.

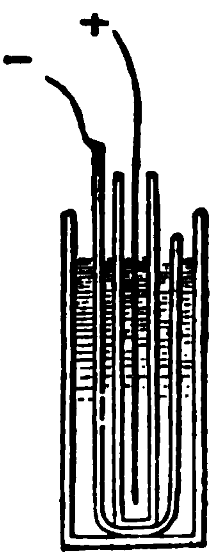
Fig. 130.

instrument of immense value for the purposes of -chemical research, in which it is desired to in powerful and equable currents for many suc- hours, has been contrived by Professor Daniell 30). Each cell of this "constant" battery con- of a copper cylinder $3\frac{1}{2}$ inches in diameter, and eight varying from 6 to 18 inches. The zinc is yed in the form of a rod $\frac{3}{4}$ of an inch in diameter, lly amalgamated, and suspended in the centre of linder. A second cell of porous earthenware or l membrane intervenes between the zinc and the r; this is filled with a mixture of 1 part by mea- f oil of vitriol and 8 of water, and the exterior with the same liquid, saturated with sulphate of r. A sort of little colander is fitted to the top of l, in which crystals of the sulphate of copper are placed, so that the

strength of the solution may remain unimpaired. When a commu made by a wire between the rod and the cylinder, a powerful curr duced, the power of which may be increased to any extent, by co sufficient number of such cells into a series, on the principle of of cups, the copper of the first being attached to the zinc of tl Ten such alternations constitute a very powerful apparatus, whi great advantage of retaining its energy undiminished for a lengthen For the copper plates become covered with a compact precipitate without the evolution of any hydrogen, so long as the solution o of copper remains saturated. By this most excellent arrangemei faces of the copper plates retain their original chemical properties u The polarization is avoided, and the chief cause of the gradual los is removed.

Mr. Grove, on precisely the same principles, succeeded afterwar ing a zinc and platinum battery, the action of wh stant. To hinder the evolution of hydrogen on num plates he employed the oxidizing action of n

Fig. 131.



One of the cells in this battery is represent margin, in section (fig. 131). The zinc plate is b so as to present a double surface, and well ama within it stands a thin flat cell of porous earthen with strong nitric acid, and the whole is imm mixture of 1 part by measure of oil of vitriol water, contained either in one of the cells of W trough, or in a separate cell of glazed porcelain the purpose. The apparatus is completed by a platinum foil which dips into the nitric acid, and positive side of the arrangement. With ten s experiments of decomposition, ignition of wires, between charcoal points, &c., can be exhibited w brilliancy, while the battery itself is very con portable, and, to a great extent, constant in its action. The zinc case of Professor Daniell's battery, is only consumed while tl passes, so that the apparatus may be arranged an hour or two l required for use, which is often a matter of great convenience. ' acid suppresses the whole of the hydrogen, becoming thereby slo dized and converted into nitrous acid, which at first remains diss after some time begins to be disengaged from the porous cells in fumes; this constitutes the only serious drawback to this excell ment.

Professor Bunsen has modified the Grove battery by substituti platinum, dense charcoal or coke, which is an excellent conduct tricity. By this alteration, at a very small expense, a battery ma as powerful and useful as that of Grove. On account of its chea one may put together one hundred or more of Bunsen's cells; by most magnificent phenomena of heat and light may be obtained.

Mr. Smee has contrived an ingenious battery, in which silver co a thin coating of finely-divided metallic platinum is employed in a with amalgamated zinc and dilute sulphuric acid. The rough surfa to permit the ready disengagement of the bubbles of hydrogen.

Within the last nine or ten years, several very beautiful and applications of voltaic electricity have been made, which may b mentioned. Mr. Spencer and Professor Jacobi have employed it in or rather in multiplying, engraved plates and medals, by deposi their surfaces a thin coating of metallic copper, which, when sepa the original, exhibits, in reverse, a most faithful representation of

e in its turn as a mould or matrix, an absolutely perfect *fac-*
plate or medal is obtained. In the former case,
ons taken on paper are quite indistinguishable from
y derived from the work of the artist; and as there
the number of *electrotype* plates which can be thus
gravings of the most beautiful description may be
definitely. The copper is very tough, and bears
the press perfectly well.

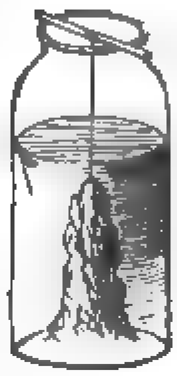
Fig. 132.

ratus used in this and many similar processes is
lest possible kind. A trough or cell of wood (fig.
ded by a porous diaphragm, made of a very thin
amore, into two parts; dilute sulphuric acid is put
and a saturated solution of sulphate of copper,
mixed with a little acid, on the other. A plate of
red to a wire or strap of copper, the other end of
cured by similar means to the engraved copper
latter is then immersed in the solution of sulphate,
in the acid. To prevent deposition of copper on the back of
plate, that portion is covered with varnish. For medals and
a porous earthenware cell, placed in a jelly-jar, may be used.
als may be precipitated in the same manner, in a smooth and
n, by the use of certain precautions which have been gathered
e. Electro-gilding and plating are now carried on very largely
perfection by Messrs. Elkington and others. Even non-conduct-
s sealing-wax and plaster of Paris, may be coated with metal;
cessary, as Mr. Murray has shown, to rub over them the thin-
e film of plumbago. Seals may thus be copied in a very few
nerring truth.

erel, several years ago, published an exceedingly interesting ac-
tain experiments, in which crystallized metals, oxides, and other
bstances had been produced by the slow and continuous action
ctrical currents, kept up for months, or even years. These pro-
ly resembled natural minerals, and, indeed, the experiments
light on the formation of the latter within the earth.[1]

non but very pleasing experiment of the *lead tree* is greatly de-
electro-chemical action. When a piece of zinc is
n a solution of acetate of lead, the first effect is
sition of a portion of the latter, and the deposi-
llic lead upon the surface of the zinc; it is simply
ent of a metal by a more oxidable one. The
s not, however, stop here; metallic lead is still
large and beautiful plates upon that first thrown
the solution becomes exhausted, or the zinc en-
pears. (Fig. 133.) The first portions of lead form
a voltaic arrangement of sufficient power to de-
salt, under the peculiar circumstances in which
placed, the metal is precipitated upon the nega-
, that is, the lead, while the oxygen and acid are
the zinc.

Fig. 133.



Grove has contrived a battery, in which an elec-
nt, of sufficient intensity to decompose water, is produced by the
oxygen upon hydrogen. Each *element* of this interesting appa-
ts of a pair of glass tubes to contain the gases, dipping into a
cidulated water. Both tubes contain platinum plates, covered

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[1] *Traité de l'Electricité* et du Magnétisme, iii. 239.

with a rough deposit of finely-divided platinum, and furnished with conducting wires, which pass through the tops or sides of the tubes, and are hermetically sealed into the latter. When the tubes are charged with oxygen on the one side and hydrogen on the other, and the wires connected with a galvanoscope, the needle of the instrument becomes instantly affected; and when ten or more are combined in a series, the oxygen-tube of the one with the hydrogen-tube of the next, &c., while the terminal wires dip into acidulated water, a rapid stream of minute bubbles from either wire indicates the decomposition of the liquid; and when the experiment is made with a small voltameter, it is found that the oxygen and hydrogen disengaged, exactly equal in amount the quantities absorbed by the act of combination in each tube of the battery.

CHEMISTRY OF THE METALS.

metals constitute the second and larger group of elementary bodies t number of these are of very rare occurrence, being found only in a rce minerals; others are more abundant, and some few almost uni- r diffused throughout the whole globe. Some of these bodies are of nportance when in the metallic state; others, when in combination, as oxides, the metals themselves being almost unknown. Many are medicine and in the arts, and are essentially connected with the pro- f civilization.

senic and tellurium be included, the metals amount to forty-nine in r.

ical Properties. — One of the most remarkable and striking characters ed by the metals is their peculiar lustre; this is so characteristic, that pression metallic lustre has passed into common speech. This pro- s no doubt connected with the extraordinary degree of opacity which tals present in every instance. The thinnest leaves or plates, the edges talline laminæ, arrest the passage of light in the most complete man- An exception to this rule is usually made in favour of gold-leaf, which eld up to the daylight exhibits a greenish colour, as if it were really with a certain degree of translucency; the metallic film is, however, so imperfect, that it becomes difficult to say whether the observed nay not be in some measure due to multitudes of little holes, many of are visible to the naked eye.

oint of colour, the metals present a certain degree of uniformity; with ceptions, viz. copper, which is red, and gold, which is yellow, all these are included between the pure white of silver, and the bluish-grey lead; bismuth, it is true, has a pinkish colour, but it is very feeble. differences of specific gravity are very wide, passing from potassium odium, which are lighter than water, to platinum, which is nearly -one times heavier than an equal bulk of that fluid.

Table of the Specific Gravities of Metals at 60° (15°·5C).[1]

Platinum	20·98
Gold	19·26
Tungsten	17·60
Mercury	13·57
Palladium	11·30 to 11·8
Lead	11·35
Silver	10·47
Bismuth	9·82
Uranium	9·00
Copper	8·89
Cadmium	8·60

[1] *Dr. Turner's Elements*, eighth edition, p. 345.

tuent metals: their properties often differ completely from those of the latter.

The oxides of the metals may be divided, as already pointed out, into three classes: namely, those which possess basic characters more or less marked, those which refuse to combine with either acids or alkalis, and those which have distinct acid properties. The strong bases are all protoxides; they contain single equivalents of metal and oxygen; the weaker bases are usually sesquioxides, containing metal and oxygen in the proportion of two equivalents of the former to three of the latter: the peroxides or neutral compounds are still richer in oxygen, and, lastly, the metallic acids contain the maximum proportion of that element.

The gradual change of properties by increasing proportions of oxygen is well illustrated by the case of manganese.

	Metal.	Oxygen.	Symbols.	Characters.
Protoxide	1 eq.	1 eq.	MnO	Strongly basic.
Sesquioxide	2 eq.	3 eq.	Mn_2O_3	Feebly basic.
Binoxide	1 eq.	2 eq.	MnO_2	Neutral.
Manganic acid	1 eq.	3 eq.	MnO_3	Strongly acid.
Permanganic acid	2 eq.	7 eq.	Mn_2O_7	Strongly acid.

The oxides of iron and chromium present similar, but less numerous gradations.

When a powerful oxygen-acid and a powerful metallic base are united in such proportions that they exactly destroy each other's properties, the resulting salt is said to be neutral; it is incapable of affecting vegetable colours. Now, in all these well-characterized neutral salts, a constant and very remarkable relation is observed to exist between the quantity of oxygen in the base, and the quantity of *acid* in the salt. This relation is expressed in the following manner:—To form a neutral combination, as many equivalents of acid must be present in the salt as there are of oxygen in the base itself. In fact, this has become the very definition of neutrality, as the action on vegetable colours is sometimes an unsafe guide.

It is easy to see the application of this law. When a base is a protoxide, a single equivalent of acid suffices to neutralize it; when a sesquioxide, not less than three are required. Hence, if by any chance, the base of a salt should pass by oxidation from the one state to the other, the acid will be insufficient in quantity by one-half to form a neutral combination. Sulphate of the protoxide of iron offers an example; when a solution of this substance is exposed to the air, it absorbs oxygen, and a yellow insoluble *sub-salt*, or *basic-salt*, is produced, which contains an excess of base. Four equivalents of the green compound absorb from the air two equivalents of oxygen, and give rise to one equivalent of neutral and one equivalent of basic sulphate of the sesquioxide, as indicated by the diagonal zigzag line of division.

1 eq. iron + 1 eq. oxygen .... 1 eq. sulphuric acid.
1 eq. iron + 1 eq. oxygen .... 1 eq. sulphuric acid.
+ 1 eq. oxygen from air
1 eq. iron + 1 eq. oxygen............ 1 eq. sulphuric acid.
1 eq. iron + 1 eq. oxygen............ 1 eq. sulphuric acid.
+ 1 eq. oxygen from air.

Such sub-salts or basic salts are very frequently insoluble.

The combinations of chlorine, iodine, bromine, and fluorine with the metals possess in a very high degree the saline character. If, however, the definition formerly given of a salt be rigidly adhered to, these bodies must be excluded from the class, and with them the very substance from which the name is

ved, that is, common salt, which is a chloride of sodium. To obviate anomaly, it has been found necessary to create two classes of salts; in first division will stand those constituted after the type of common salt, h contain a metal and a *salt-radical*, as chlorine, iodine, &c.; and in the nd, those which, like sulphate of soda and nitrate of potassa, are gene- supposed to be combinations of an acid with an oxide. The names id[1] *salts*, and *oxygen-acid*, or *oxy-salts*, are given to these two kinds.

hen a haloid salt is dissolved in water, it might be regarded as a combi- on of a metallic oxide with a hydrogen-acid, the water being supposed ndergo decomposition, its hydrogen being transferred to the salt-radical, its oxygen to the metal. This view is unsupported by evidence of any e: it is much more probable, indeed, that no truly saline compounds of rogen-acids exist, at any rate in inorganic chemistry. When a solution ny hydrogen-acid is poured upon a metallic oxide, we may rather suppose both are decomposed, water and a haloid salt of the metal being pro- ed. Take hydrochloric acid and potassa by way of example.

Hydrochloric acid	Chlorine	Chloride of potassium.
	Hydrogen	
Potassa	Potassium	
	Oxygen	Water.

n evaporating the solution, the chloride of potassium crystallizes out.

hen hydrochloric acid and ammoniacal gases are mixed, they combine some energy and form a white solid salt, sal-ammoniac. Now this sub- ce bears such a strong resemblance in many important particulars to ride of potassium and common salt, that the ascription to it of a similar itution is well warranted.

chloride of potassium, therefore, contain chlorine and metal, sal-ammo- may also contain chlorine in combination with a substance having the mical relations of a metal, formed by the addition of the hydrogen of the l to the elements of the ammonia.

Hydrochloric acid	1 eq. Chlorine	Chlorine ...	Sal-ammoniac.
	1 eq. Hydrogen		
Ammonia ...	3 eq. Hydrogen		
	1 eq. Nitrogen	Ammonium	

he term *ammonium* is given to this hypothetical body, NH_4; it is sup- d to exist in all the ammoniacal salts. Thus we have chloride of nonium, sulphate of the oxide of ammonium, &c. This view is very ngly supported by the peculiarities of the salts themselves, and by the tence of a series of substances intimately related to these salts in organic mistry, as will hereafter be seen.

lany of the sulphides also possess the saline character and are soluble in er, as those of potassium and sodium. Sometimes a pair of sulphides unite in definite proportions, and form a crystallizable compound. Such ies bear a very close resemblance to oxygen-acid salts; they usually tain a protosulphide of an alkaline metal, and a higher sulphide of a non- allic substance or of a metal which has little tendency to form a basic le, the two sulphides having exactly the same relation to each other as oxide and acid of an ordinary salt. Hence the expressions *sulphur-salt*, *hur-acid*, and *sulphur-base*, which Berzelius applies to such compounds; contain sulphur in the place of oxygen. Thus, bisulphide of carbon is lphur-acid; it forms a crystallizable compound with protosulphide of ssium, which is a sulphur-base. Were oxygen substituted for the sulphur his product, we should have carbonate of potassa.

[1] ἅλς, sea-salt, and εἶδος, form.

$KS + CS_2$ sulphur-salt.
$KO + CO_2$ oxygen-salt.

These remarkable compounds are very numerous and interesting; they have been studied by Berzelius with great care.

Salts often combine together, and form what are called *double salts*, in which the same acid is in combination with two different bases. When sulphate of copper and sulphate of potassa, or chloride of zinc and sal-ammoniac, are mixed in the ratio of the equivalents, dissolved in water, and the solution made to crystallize, double salts are obtained. These latter are often more beautiful, and crystallize better than their constituent salts.

Many of the compounds called *super*, or *acid salts*, such as bisulphate of potassa, which have a sour taste and acid reaction to test-paper, ought strictly to be considered in the light of double salts, in which one of the bases is water. Strange as it may at first sight appear, water possesses considerable basic powers, although it is unable to mask acid reaction on vegetable colours: hydrogen, in fact, very much resembles a metal in its chemical relations. Bisulphate of potassa will, therefore, be a double sulphate of potassa and water, while oil of vitriol must be assimilated to neutral sulphate of potassa.

$KO + SO_3$ and $HO + SO_3$.

Water is a weak base: it is for the most part easily displaced by a metallic oxide: yet cases occur now and then in which the reverse happens, and water is seen to decompose a salt, in virtue of its basic power.

There are few acid salts which contain no water; as the bichromate of potassa, and a new anhydrous sulphate of potassa discovered by M. Jacquelain.[1] It will be necessary, of course, to adopt some other view in these cases. The simplest will be to consider them as really containing two equivalents of acid to one of base.

By *water of crystallization* is meant water in a somewhat loose state of combination with a salt, or other compound body, from which it can be disengaged by the mere application of heat, or by exposure to a dry atmosphere. Salts which contain water of crystallization have their crystalline form greatly influenced by the proportion of the latter. Green sulphate of iron crystallizes in two different forms, and with two different proportions of water, according to the temperature at which the salt separates from the solution.

Many salts containing water *effloresce* in a dry atmosphere, crumbling to powder, and losing part or the whole of their water of crystallization; while in a moist atmosphere they may be preserved unchanged. The opposite effect to this, or *deliquescence*, results from a strong attraction of the salt for water, in virtue of which it absorbs the latter from the air, often to the extent of liquefaction.

Crystallization: Crystalline Forms.—Almost every substance, simple and compound, capable of existence in the solid state, assumes, under favourable circumstances, a distinct geometrical form or figure, usually bounded by plane surfaces, and having angles of fixed and constant value. The faculty of crystallization seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand, as it were, upon the very edge of organization, and which, when in a solid state, are frequently characterized by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallization are to be found among natural minerals, the result of exceedingly slow changes constantly occurring within the earth; it is invariably found that artificial crystals of salts, and

[1] Ann. Chim. et Phys. lxx. 311.

luble substances, which have been slowly and quietly deposited, urpass in size and regularity those of more rapid formation.

on in water or some other liquid is one very frequent method of crystallization. If the substance be more soluble at a high than at temperature, then a hot and saturated solution by slow cooling will r be found to furnish crystals; this is a very common case with salts ous organic principles. If it be equally soluble, or nearly so, at all ures, then slow spontaneous evaporation in the air, or over a suril of vitriol, often proves very effective.

and slow cooling may be employed in many cases; that of sulphur d example; the metals usually afford traces of crystalline figure us treated, which sometimes become very beautiful and distinct, as nuth. A third condition under which crystals very often form is in from a gaseous to a solid state, of which iodine affords a good in- When by any of these means time is allowed for the symmetrical nent of the particles of matter at the moment of solidification, are produced.

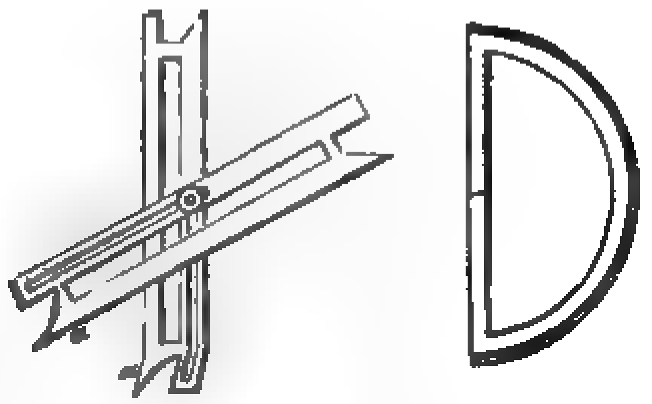
rystals owe their figure to a certain regularity of internal structure, both by their mode of formation and also by the peculiarities at- their fracture. A crystal placed in a slowly-evaporating saturated of the same substance grows or increases by a continued deposition matter upon its sides in such a manner that the angles formed by ing of the latter remain unaltered.

endency of most crystals to split in particular directions, called by gists *cleavage*, is a certain indication of regular structure, while the optical properties of many among them, and their remarkable mode sion by heat, point to the same conclusion.

r be laid down as a general rule that every substance has its own ne form, by which it may very frequently be recognized at once; each substance has a different figure, although very great diversity espect is to be found. Some forms are much more common than s the cube and six-sided prism, which are very frequently assumed nber of bodies, not in any way related.

ame substance may have, under different sets of circumstances, as l low temperatures, two different crystalline forms, in which case it s be *dimorphous*. Sulphur and carbon furnish, as already noticed, s of this curious fact; another case is presented by carbonate of he two modifications of calcareous spar and arragonite, both chemi- same, but physically different. A fourth example might be given dide of mercury, which also has two distinct forms, and even two colours, offering as great a contrast as those of diamond and plum-

Fig. 125.

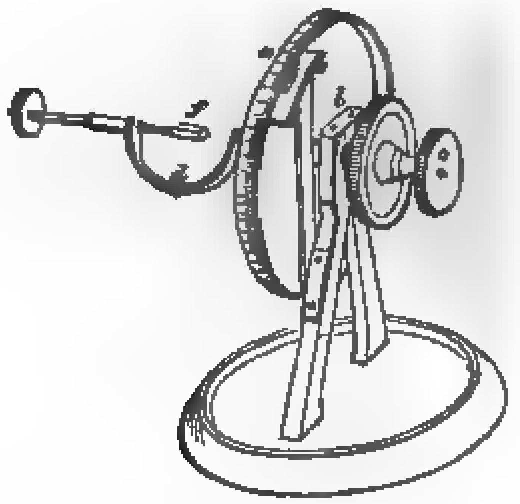


The angles of crystals are measured by means of instruments called *goniometers*, of which there are two kinds in use, namely, the old or common goniometer, and the reflective goniometer of Dr. Wollaston.

The common goniometer consists of a pair of steel blades moving with friction upon a centre, as shown in the cut (fig. 185). The edges *a a* are carefully adjusted to the faces of the crystal, whose inclination to each other it is required to ascertain, and then the instrument being applied to the divided semicircle, the contained angle is at once read off. An approximative measurement, within one or two degrees, can be easily obtained by this instrument, provided the planes of the crystal be tolerably perfect, and large enough for the purpose. Some practice is of course required before even this amount of accuracy can be attained.

The reflective goniometer is a very superior instrument, its indications being correct within a fraction of a degree; it is applicable also to the measurement of the angles of crystals of very small size, the only condition required being that their planes be smooth and brilliant. The subjoined sketch (fig. 136) will convey an idea of its nature and mode of use.

Fig. 136.



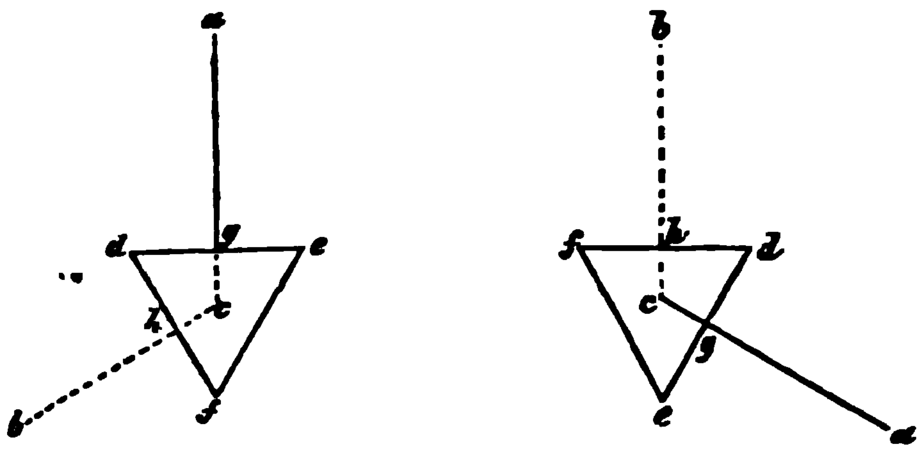
a is a divided circle or disc of brass, the axis of which passes stiffly and without shake through the support *b*. This axis is itself pierced to admit the passage of a round rod or wire, terminated by the milled-edged head *c*, and destined to carry the crystal to be measured by means of the jointed arm *d*. A vernier, *e*, immovably fixed to the upright support, serves to measure with great accuracy the angular motion of the divided circle. The crystal at *f* can thus be turned round, or adjusted in any desired position, without the necessity of moving the disc.

The principle upon which the measurement of the angle rests is very simple. If the two adjacent planes of a crystal be successively brought into the same position, the angle through which the crystal will have moved will be *the supplement to that contained between the two planes.* This will be easily intelligible by reference to fig. 137, in which a crystal having the form of a triangular prism[1] is shown in the two positions, the angle to be measured being that indicated by the letters *e d f*.

The lines *a c*, *b c*, are perpendicular to the respective faces of the crystal,

[1] *The triangular prism has been chosen for the sake of simplicity; but a moment's consideration will show that the rule applies equally well to any other figure.*

Fig. 137.



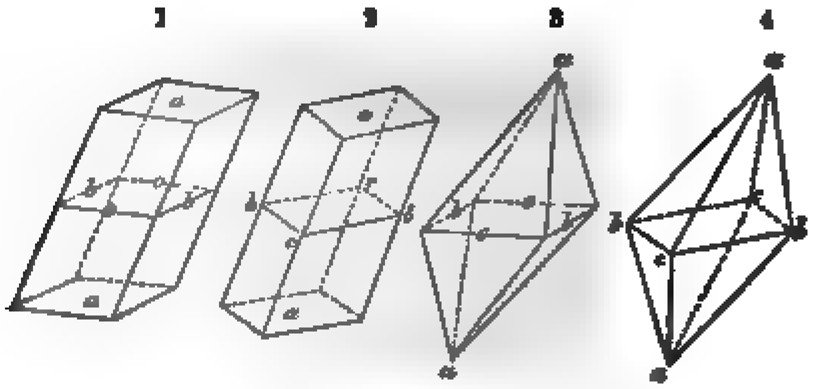
quently the internal angles $d\,g\,c$, $d\,h\,c$, are right angles. Now, since um of the internal angles of a four-sided rectilineal figure, as $d\,g\,c\,h$, *four* right angles, or 360°, the angle $g\,d\,h$ (or $e\,d\,f$) must of necessity ie supplement to the angle $g\,c\,h$, or that through which the crystal s. All that is required to be done, therefore, is to measure the latter with accuracy, and subtract its value from 180°; and this the gonio- r effects.

e method of using the instrument is the following:—The goniometer is d at a convenient height upon a steady table in front of a well-illumi- l window. Horizontally across the latter, at the height of eight or nine from the ground, is stretched a narrow black ribbon, while a second ar ribbon, adjusted parallel to the first, is fixed beneath the window, a or eighteen inches above the floor. The object is to obtain too easily- e black lines, perfectly parallel. The crystal to be examined is attached e arm of the goniometer at f by a little wax, and adjusted in such a ier that the edge joining the two planes whose inclination is to be mea- l shall nearly coincide with, or be parallel to, the axis of the instru- . This being done, the adjustment is *completed* in the following manner: e divided circle is turned until the zero of the vernier comes to 180°; rystal is then moved round by means of the inner axis c (fig. 136) until ye placed near it perceives the image of the upper black line reflected the surface of one of the planes in question. Following this image, rystal is still cautiously turned until the upper black line seen by re- m approaches and overlaps the lower black line seen *directly* by another m of the pupil. It is obvious, that if the plane of the crystal be quite lel to the axis of the instrument (the latter being horizontal), the two will coincide completely. If, however, this should not be the case, the l must be moved upon the wax until the two lines fall in one when su- sed. The second face of the crystal must then be adjusted in the same er, care being taken not to derange the position of the first. When by ted observation it is found that both have been correctly placed, so as ng the edge into the required condition of parallelism with the axis of n, the measurement of the angle may be made.

this purpose the crystal is moved as before by the inner axis until the of the upper line, reflected from the first face of the crystal covers wer line seen directly. The great circle, carrying the whole with it, n cautiously turned until the same coincidence of the upper with the line is seen by means of the second face of the crystal; that is, the d face is brought into exactly the same position as that previously ied by the first. Nothing then remains but to read off by the vernier gle through which the circle has been moved in this operation. The *n upon the circle itself* is very often made *backwards*, so that the

be all unequal in length, and are all oblique to each other, as in th *doubly-oblique prisms* (1 and 2), and in the corresponding *doubly-obliqu hedrons* (3 and 4).

Fig. 142.

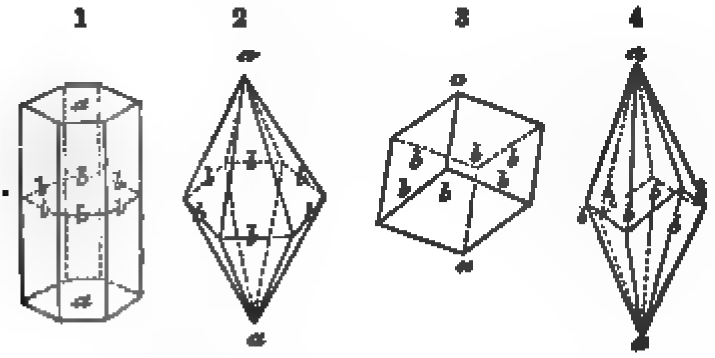


a—a. Principal axis, as before.
b—b, c—c. Secondary axes.

Sulphate of copper, nitrate of bismuth, and quadroxalate of potassa, illustrations of these forms.

6. *The rhombohedral system.*—This is very important and extensive characterized by the presence of *four* axes, three of which are equal, same plane, and inclined to each other at angles of 60°, while the fo

Fig. 143.



a—a. Principal axis.
b—b. Secondary axes.

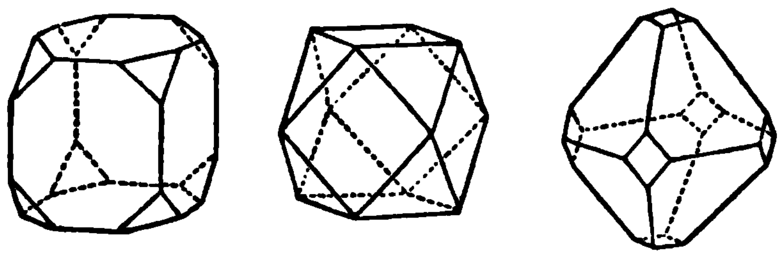
principal axis is perpendicular to all. The *regular six-sided prism* (*quartz-dodecahedron* (2), the *rhombohedron* (3), and a *second* dodecah whose faces are scalene triangles (4), belong to the system in questio

Examples are readily found; as in ice, calcareous spar, nitrate of beryl, quartz or rock crystal, and the semi-metals, arsenic, antimon tellurium.

If a crystal increase in magnitude by equal additions on every par quite clear that its figure must remain unaltered; but, if from some this increase should be partial, the newly-deposited matter being distr unequally, but still in obedience to certain definite laws, then alterati form are produced, giving rise to figures which have a direct geom connection with that from which they are derived. If, for example, cube, a regular omission of successive rows of particles of matter in tain order be made at each solid angle, while the crystal continues to in *elsewhere*, the result will be the production of small triangular p

which, as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octahedron. The new planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube; a new figure, the rhombic dodecahedron, is then generated. Fig. 144. The modifications which can thus be produced of the original or *primary* figure (all of which are subject to exact geometrical laws) are very numerous. Several distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Fig. 144.



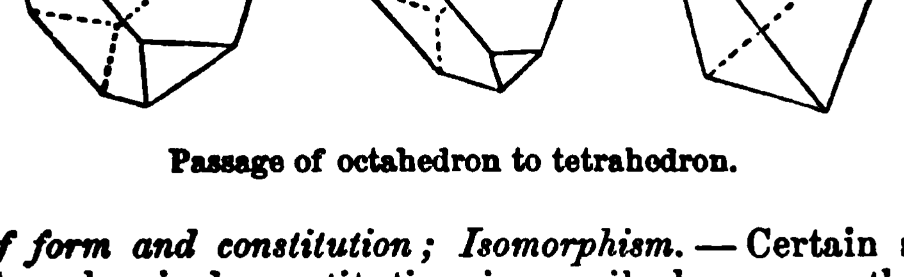
Passage of cube to octahedron.

It is important to observe, that in all these deviations from what may be regarded as the primary or fundamental figure of the crystal, the modifying planes are in fact *the planes of figures belonging to the same natural group or crystallographical system as the primary form, and having their axes coincident with those of the latter.* The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

Crystals often cleave parallel to all the planes of the primary figure, as in calcareous spar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at length obliterated, and the crystal assumes the character called *hemihedral* or *half-sided.* This is well seen in the production of the tetrahedron from the regular octahedron (fig. 145), and of the rhombohedric form by a similar change from the quartz-dodecahedron already figured.

Fig. 145.



Passage of octahedron to tetrahedron.

Relations of form and constitution; Isomorphism. — Certain substances to which a similar chemical constitution is ascribed, possess the remarkable property of exactly replacing each other in crystallized compounds without alteration of the characteristic geometrical figure. Such bodies are said to be *isomorphous.*[1]

[1] *From* ἴσος, equal, and μόρφη, shape or form.

For example, magnesia, oxide of zinc, oxide of copper, protoxide of iron, and oxide of nickel, are allied by isomorphic relations of the most intimat nature. The salts formed by these substances with the same acid an similar proportions of water of crystallization, are identical in their form and, when of the same colour, cannot be distinguished by the eye; the sul phates of magnesia and zinc may be thus confounded. The sulphates, too all combine with sulphate of potassa and sulphate of ammonia, giving ri to double salts, whose figure is the same, but quite different from that of th simple sulphates. Indeed, this connection between identity of form an parallelism of constitution runs through all their combinations.

In the same manner, alumina and sesquioxide of iron replace each oth continually without change of crystalline figure; the same remark may l made of potassa, soda, and ammonia, with an equivalent of water, or oxi of ammonium, these bodies being strictly isomorphous. The alumina i in common alum may be replaced by sesquioxide of iron; the potassa l ammonia, or by soda, and still the figure of the crystal remains unchange These replacements may be partial only; we may have an alum containi both potassa and ammonia, or alumina and sesquioxide of chromium. I artificial management, namely, by transferring the crystal successively different solutions, we may have these isomorphous and mutually replaci compounds distributed in different layers upon the same crystal.

For these reasons, mixtures of isomorphous salts can never be separat by crystallization, unless their difference of solubility is very great. mixed solution of sulphate of protoxide of iron and sulphate of copper, is morphous salts, yields on evaporation crystals containing both iron a copper. But if before evaporation the protoxide of iron be converted in sesquioxide by chlorine or other means, then the crystals obtained are fr from iron, except that of the mother-liquor which wets them. The salt sesquioxide of iron is no longer isomorphous with the copper salt, and eas separates from the latter.

When compounds are thus found to correspond, it is inferred that the e ments composing them are also isomorphous. Thus, the metals magnesiu zinc, iron, and copper are presumed to be isomorphous; arsenic and ph phorus should present the same crystalline form, because arsenic and ph phoric acids give rise to combinations which agree most completely in figu and constitution. The chlorides, iodides, bromides, and fluorides, agr whenever they can be observed, in the most perfect manner; hence the e ments themselves are believed to be also isomorphous. Unfortunately, obvious reasons, it is very difficult to observe the crystalline figure of m of the elementary bodies, and this difficulty is increased by the frequent morphism they exhibit.

Absolute identity of value in the angles of crystals is not always exhibi by isomorphous substances. In other words, small variations often oc in the magnitude of the angles of crystals of compounds which in all ot respects show the closest isomorphic relations. This should occasion surprise, as there are reasons why such variations may be expected, chief perhaps being the unequal effects of expansion by heat, by which angles of the same crystals are changed by alteration of temperature. good example is found in the case of the carbonates of lime, magnesia, m ganese, iron, and zinc, which are found native crystallized in the form obtuse rhombohedra (fig. 143, 3) not distinguishable from each other by eye, or even by the common goniometer, but showing small differences wh examined by the more accurate instrument of Dr. Wollaston. These co pounds are isomorphous, and the measurements of the obtuse angles of th rhombohedra as follows:—

Carbonate of	lime	105° 5′
"	magnesia	107° 25′
"	protox. manganese	107° 20′
"	" iron	107°
"	zinc	107° 40′

nomalies in the composition of various earthy minerals which formerly w much obscurity upon their chemical nature, have been in great mea- explained by these discoveries.

pecimens of the same mineral from different localities were found to d very discordant results on analysis. But the proof once given of the nt to which substitution of isomorphous bodies may go without destruc- of what may be called the primitive type of the compound, these diffi- es vanish.

nother benefit conferred on science by the discoveries in question, is of furnishing a really philosophical method of classifying elementary compound substances, so as to exhibit their natural relationships: it ld be perhaps more proper to say that such will be the case when the orphic relations of all the elementary bodies become known,—at present a certain number have been traced.

ecision of a doubtful point concerning the constitution of a compound now and then be very satisfactorily made by a reference to this same of isomorphism. Thus, alumina, the only known oxide of aluminium, dged to be a sesquioxide of the metal from its relation to sesquioxide ron, which is certainly so; the black oxide of copper is inferred to be ly the protoxide, although it contains twice as much oxygen as the red e, because it is isomorphous with magnesia and zinc, both undoubted oxides.

he subjoined table will serve to convey some idea of the most important ilies of isomorphous elements; it is taken from Professor Graham's sys- atic work,[1] to which the pupil is referred for fuller details on this inte- ing subject.

Isomorphous Groups.

(1.)	(3.)	(7.)
Sulphur	Barium	Sodium
Selenium	Strontium	Silver
Tellurium.	Lead.	Gold
(2.)	(4.)	Potassium
Magnesium	Tin	*Ammonium.*
Calcium	Titanium.	(8.)
Manganese	(5.)	Chlorine
Iron	Platinum	Iodine
Cobalt	Iridium	Bromine
Nickel	Osmium.	Fluorine
Zinc	(6.)	*Cyanogen.*
Cadmium	Tungsten	(9.)
Copper	Molybdenum	Phosphorus
Chromium	Tantalum.	Arsenic
Aluminium		Antimony
Beryllium		Bismuth.
Vanadium		
Zirconium.		

here is a law concerning the formation of double salts which may now mentioned; the two bases are never taken from the same isomorphous

[1] Second edition, p. 149.

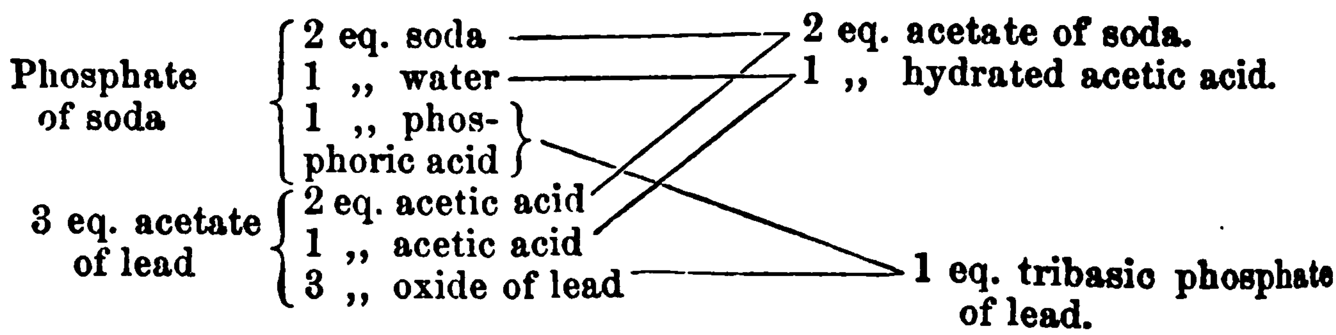
family. Sulphate of copper or of zinc may unite in this manner with sulphate of soda or potassa, but not with sulphate of iron or cobalt; chloride of magnesium may combine with chloride of ammonium, but not with chloride of zinc or nickel, &c. It will be seen hereafter that this is a matter of some importance in the theory of the organic acids.

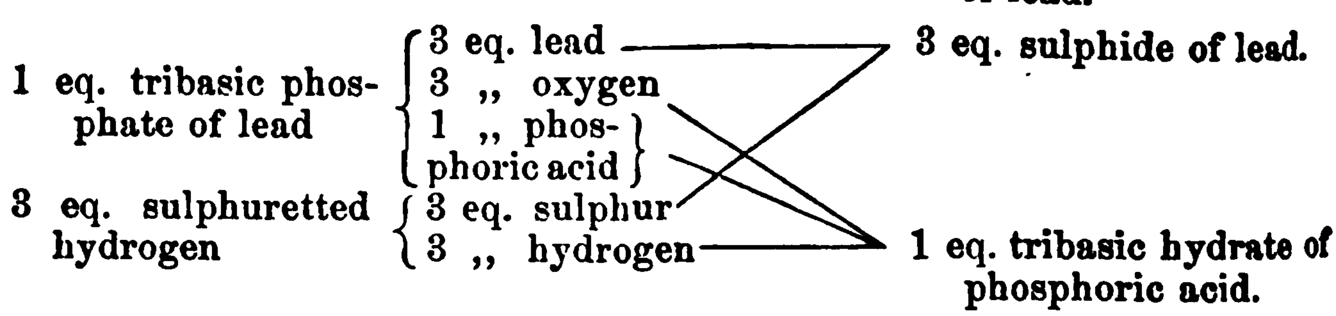
Polybasic Acids. — There is a particular class of acids in which a departure occurs from the law of neutrality formerly described; these are acids requiring two or more equivalents of a base for neutralization. The phosphoric and arsenic acids present the best examples yet known in mineral chemistry, but in the organic department of the science cases very frequently occur.

Phosphoric acid is capable of existing in three different states or modifications, forming three separate classes of salts which differ completely in properties and constitution. They are distinguished by the names *tribasic*, *bibasic*, and *monobasic* acids, according to the number of equivalents of base required to form neutral salts.

Tribasic or *Common Phosphoric Acid.* — When commercial phosphate of soda is dissolved in water and the solution mixed with acetate of lead, an abundant white precipitate of phosphate of lead falls, which may be collected on a filter, and well washed. While still moist, this compound is suspended in distilled water, and an excess of sulphuretted hydrogen gas passed into it. The protoxide of lead is converted into sulphide, which subsides as a black insoluble precipitate, while phosphoric acid remains in solution, and is easily deprived of the residual sulphuretted hydrogen by a gentle heat.

The soda-salt employed in this experiment contains the tribasic modification of phosphoric acid; of the three equivalents of base, two consist of soda and one of water; when mixed with solution of lead, a tribasic phosphate of the oxide of that metal falls, which when decomposed by sulphuretted hydrogen, yields sulphide of lead and a hydrate of the acid containing three equivalents of water in intimate combination.





The solution of tribasic hydrate may be concentrated by evaporation *in vacuo* over sulphuric acid until it crystallizes in thin deliquescent plates. The same compound in beautiful crystals, resembling those of sugar-candy, has been accidentally formed.[1] It undergoes no change by boiling with water, but when heated alone to 400° (204°·4C) loses some of its combined water, and becomes converted into a mixture of the bibasic and monobasic hydrates. At a red heat it becomes entirely changed to monohydrate, which, at a still higher temperature, sublimes.

Tribasic phosphoric acid is characterized by the yellow insoluble salt it forms with protoxide of silver.

[1] Péligot, Ann. Chim. et Phys. lxxiii. 286.

Bibasic Phosphoric Acid, or *Pyrophosphoric Acid.*—When common phosphate of soda, containing

$$2NaO, HO, PO_5+24HO,$$

gently heated, the 24 equivalents of water of crystallization are expelled, and the salt becomes anhydrous; but if the heat be raised to a higher point, the basic water is also driven off, and the acid passes into the second or bibasic modification. If the altered salt be now dissolved in water, this new compound, the bibasic phosphate of soda, crystallizes out. When mixed with solution of acetate of lead, bibasic phosphate of lead is thrown down, which, decomposed by sulphuretted hydrogen, furnishes a solution of the bibasic hydrate. This solution may be preserved without change at common temperatures, but when heated, an equivalent of water is taken up, and the substance passes back again into the tribasic modification.

Crystals of this hydrate have also been observed by M. Péligot. Their production was accidental. The bibasic phosphates soluble in water give a white precipitate with solution of silver.

Monobasic, or Metaphosphoric Acid.—When common tribasic phosphate of soda is mixed with solution of tribasic hydrate of phosphoric acid, and exposed, after proper concentration, to a low temperature, prismatic crystals are obtained, which consist of a phosphate of soda having two equivalents of basic water.

$$NaO, 2HO, PO_5+2HO.$$

When this salt is very strongly heated, both the water of crystallization and that contained in the base are expelled, and monobasic phosphate of soda remains. This may be dissolved in cold water, precipitated with acetate of lead, and the lead-salt, as before, decomposed by sulphuretted hydrogen.

The solution of the monobasic hydrate is decomposed rapidly by heat, becoming converted into tribasic hydrate. It possesses the property of coagulating albumen, which is not enjoyed by either of the preceding modifications. Monobasic alkaline phosphates precipitate nitrate of silver white.

The glacial phosphoric acid of pharmacy is, when pure, hydrate of monobasic phosphoric acid: it contains HO, PO_5.

Anhydrous phosphoric acid, prepared by burning phosphorus in dry air, when thrown into water, forms a variable mixture of the three hydrates. When heated, a solution of the tribasic hydrate alone remains.[1] See also phosphates of soda.

Binary Theory of Salts.—The great resemblance in properties between the two classes of saline compounds, the haloid and oxy-salts, has very naturally led to the supposition that both might possibly be alike constituted, and that the latter, instead of being considered compounds of an oxide and an acid, might with greater propriety be considered to contain a metal in union with a compound salt-radical, having the chemical relations of chlorine and iodine.

On this supposition sulphate and nitrate of potassa will be constituted in the same manner as chloride of potassium, the compound radical replacing the simple one.

Old view.	New view.
$KO+SO_3$	$K+SO_4$
$KO+NO_5$	$K+NO_6$

[1] The three modifications of phosphoric acid possess properties so dissimilar that they might fully be considered three distinct, although intimately related bodies. It is exceedingly remarkable, that when their salts are subjected to electro-chemical decomposition, the acids travel *unaltered*, a tribasic salt giving at the positive electrode a solution of common phosphoric acid; a bibasic salt, one of pyrophosphoric acid; and a monobasic salt, one of metaphosphoric acid (Professor Daniell and Dr. Miller, Phil. Trans. for 1844, p. 1).

Hydrated sulphuric acid will be, like hydrochloric acid, a hydride of a salt radical,

$$H+SO_4.$$

When the latter acts upon metallic zinc, the hydrogen is simply displaced and the metal substituted; no decomposition of water is supposed to occur and, consequently, the difficulty of the old hypothesis is at an end. Whe the acid is poured upon a metallic oxide, the same reaction occurs as in th case of hydrochloric acid, water and a haloid salt are produced. All acid must be, in fact, hydrogen acids, and all salts haloid salts, with either simpl or compound radicals.

This simple and beautiful theory is not by any means new; it was sug gested by Davy, who proposed to consider hydrogen as the acidifying prin ciple in the common acids, and lately revived and very happily illustrated b Liebig. It is supported by a good deal of evidence derived from variou sources, and has received great help from a series of exceedingly interestin experiments on the electrolysis of saline solutions, by the late Professo Daniell.[1] The necessity of creating a great number of non-insoluble com pounds is often urged as an objection to the new view; but the same objec tion applies to the old mode of considering the subject. Hyposulphurou acid and hyposulphuric acid are unknown in their free states. The com pounds S_2O_2 and S_2O_4 are as hypothetical as the substances S_2O_3 and S_2O The same remark applies to almost every one of the organic acids; and, wha is well worthy of notice, those acids which, like sulphuric, phosphoric, an carbonic acids, may be obtained in a separate state, are *destitute of all ac properties so long as the anhydrous condition is retained.*

Some very interesting observations have been published lately by M. Ge hardt,[2] which are likely to hasten a change in the notation of acids generall

It has been pointed out that sulphuric and nitric acid, which, accordin to the theory of oxygen acids, are considered as compounds respectively teroxide of sulphur and pentoxide of nitrogen with water, SO_3,HO, and NO HO, may be considered likewise as hydrogen acids, analogous to hydr chloric and hydrocyanic acid.

Hydrochloric acid	HCl
Hydrocyanic acid	HC_2N
Sulphuric acid / Hydrosulphanic acid	HSO_4
Nitric acid / Hydronitranic acid	HNO_6.

Among the many facts which have been adduced in favour of the theo of oxygen acids, the preparation of the so-called anhydrous acids SO_3 a NO_5 (see pages 124 and 135) has always been considered as powerful proj On the other hand, the followers of the theory of hydrogen acids have inv riably called attention to the scarcity of the so-called anhydrous acids, a especially to the fact that, with a few exceptions, they are entirely wanti in Organic Chemistry. The researches of M. Gerhardt just referred have furnished the means of making the anhydrous organic acids; but t circumstances under which they are produced exhibit these substances in perfectly new light, and prove that they stand in a very different relation the hydrated acids from what is generally assumed.

If dry benzoate of soda be heated with chloride of benzoyl (see page 3 to a temperature of 266° (130°C), a limpid liquid is formed, which is

[1] See Daniell's Introduction to Chemical Philosophy, 2d edition, p. 533.
[2] *Chem. Soc.* Quar. Jour. v. 127.

posed with deposition of chloride of sodium when heated a few degrees ier; there is formed, at the same time, a white crystalline product, ch has exactly the composition of anhydrous benzoic acid, for it contains I_6O_3 or BzO, if we represent $C_{14}H_5O_2$ by Bz. The decomposition which es place is represented by the following equation:—

$$BzO,NaO+BzCl=NaCl+2BzO.$$

he new substance crystallizes in beautiful oblique prisms, fusible at 90°·4 °C), and volatile without decomposition. It is insoluble in water, but dily dissolves in alcohol and ether; *these solutions are perfectly neutral to paper.* Cold water has not the slightest effect upon this body; by boil- water it is gradually converted into benzoic acid. This change immedi- ly occurs with boiling solutions of the alkalis. Boiling alcohol converts nto benzoate of ethyl. From the mode of formation, it is evident that substance in question cannot be regarded as anhydrous benzoic acid, al- ugh it agrees with that substance in composition. It is obviously a sort a salt, *benzoate of benzoyl,* or benzoic acid in which one equivalent of hy- gen is replaced by benzoyl.

Benzoic acid	BzO,HO
New compound	BzO,BzO.

f an additional support for this view was required, it would be found in circumstance that chloride of benzoyl acts in exactly the same manner n cumate, cinnamate, and salicylate of soda, a series of compounds be- produced which are perfectly analogous to the preceding substance, but tain in the place of benzoyl *cuminyl,* $C_{20}H_{12}O_2$=Cm; *cinnamyl,* $C_{18}H_7O^2$= ; or *salicyl,* $C_{14}H_5O_4$=Sl.

Benzoic acid	BzO,HO
Benzoate of benzoyl	BzO,BzO
Benzoate of cuminyl	BzO,CmO
Benzoate of cinnamyl	BzO,CiO
Benzoate of salicyl	BzO,SlO.

se substances are for the most part fusible, odourless solids, or oils vier than water. With the alkalis they yield a mixture of the acids from ich they have been produced. Several are not volatile without decompo- on.

A perfectly similar series of substances has been obtained with acetic acid. acetic chloride, $ClC_4H_3O_2$, corresponding to chloride of benzoyl, is formed a most interesting process, namely, by the action of pentachloride of sphorus (see page 168) upon acetate of soda, when chloride of sodium, hloride of phosphorus, PCl_3O_2, and chloride of acetetyl[1] are formed.

$$NaO,C_4H_3O_3+PCl_5=NaCl+PCl_3O_2+C_4H_3O_2Cl.$$

he action of chloride of acetetyl upon dry acetate of soda gives rise to formation of an oily liquid, which has the composition of anhydrous tic acid, $C^4H_3O_3$, but which in reality is acetate of acetetyl=$C_4H_3O_3$, $_3O_2$,O.[2] This liquid boils at 278°·6 (137°C); it is not miscible at once

[1] Acetetyl in order to distinguish it from acetyl, C_4H_3.

[2] This formula requires an equivalent of oxygen to produce two equivalents of anhydrous c acid.

$$C_4H_3O_3,C_4H_3O_2O+O=2(C_4H_3O_3,O).$$

he reaction between acetate of soda and chloride of acetyle, an equivalent of oxygen from soda converts the acetetyl into anhydrous acetic acid with the formation of chloride of um.

$$NaO.C_4H_3O_3+C_4H_3O_2Cl=2(C_4H_3O_3)+NaCl.$$

etyle here spoken of, is from its composition acetous or aldehydic acid.—R. B.

with cold water, but only after continued agitation. Hot water dissolve at once with formation of acetic acid.

The application to inorganic compounds of the method, by means of whi these substances are produced, promises in future very important materi for the elaboration of several of the most interesting questions with whi chemists are engaged at the present moment.

The general application of the binary theory still presents a few diffic ties. But it is very probable that the progress of discovery will ultimat lead to its universal adoption, which would greatly simplify many parts the science. One great inconvenience will be the change of nomenclatu involved.

CLASSIFICATION OF METALS.

1.
Metals of the Alkalis.

Potassium,
Sodium,
Lithium,
Ammonium.[1]

2.
Metals of the Alkaline Earths.

Barium,
Strontium,
Calcium,
Magnesium.

3.
Metals of the Earths Proper.

Aluminium,
Beryllium,
Yttrium,
Erbium,
Terbium,
Zirconium,
Norium,
Thorium,
Cerium,
Lantanum,
Didymium.

4.
Oxidable Metals proper, whose Oxides form powerful Bases.

Manganese,
Iron,
Chromium,
Nickel,
Cobalt,
Copper,
Zinc,
Cadmium,
Bismuth,
Lead,
Uranium.

5.
Oxidable Metals Proper, whose Oxides form weak Bases, or Acids.

Vanadium,
Tungsten,
Molybdenum,
Tantalum,
Niobium,
Pelopium,
Titanium,
Tin,
Antimony,
Arsenic,
Tellurium,
Osmium.

6.
Metals Proper, whose Oxides are reduced by Heat; Noble Metals.

Gold,
Mercury,
Silver,
Platinum,
Palladium,
Iridium,
Ruthenium,
Rhodium.

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[1] *This hypothetical* substance is merely placed with the metals for the sake of conven *as will be* apparent in the sequel.

SECTION I.

METALS OF THE ALKALIS.

POTASSIUM.

ι was discovered by Sir H. Davy in 1807, who obtained it in uantity by exposing a piece of moistened hydrate of potassa to ' a powerful voltaic battery, the alkali being placed between a .num plates put into connection with the apparatus. Processes)een devised for obtaining this curious metal in almost any t can be desired.

te mixture of carbonate of potassa and charcoal is prepared by a covered iron pot, the crude tartar of commerce; when cold, to powder, mixed with one-tenth part of charcoal in small lumps, transferred to a retort of stout hammered iron; the latter may e iron bottles in which mercury is imported, a short and someon tube having been fitted to the aperture. The retort is placed e, in a furnace so constructed that the flame of a very strong ι dry wood, may wrap round it, and maintain every part at an ;ree of heat, approaching to whiteness. A copper receiver, .e centre by a diaphragm, is connected to the iron pipe, and kept ιpplication of ice, while the receiver itself is partly filled with ·ock-oil, in which the potassium is to be preserved. Arrange· thus completed, the fire is gradually raised until the requisite is reached, when decomposition of the alkali by the charcoal carbonic oxide gas is abundantly disengaged, and potassium and falls in large melted drops into the liquid. The pieces of introduced for the purpose of absorbing the melted carbonate nd preventing its separation from the finely divided carbonaceous

assium be wanted absolutely pure, it must be afterwards re-dis- iron retort, into which some naphtha has been put, that its expel the air, and prevent the oxidation of the metal.

is a brilliant white metal, with a high degree of lustre; at the perature of the air it is soft, and may be easily cut with a knife,)°C) it is brittle and crystalline. It melts completely at 136° nd distils at a low red heat. The density of this remarkable r 0·865, water being unity.

;o the air, potassium oxidizes instantly, a tarnish covering the ıe metal, which quickly thickens to a crust of caustic potassa. n water, it takes fire spontaneously, and burns with a beautiful , yielding an alkaline solution. When brought into contact with r in a jar standing over mercury, the liquid is decomposed with ·, and hydrogen liberated. Potassium is always preserved under ıf naphtha.

ılent of *potassium (kalium)* is 39; and its symbol, K

There are two compounds of this metal with oxygen,—potassa and teroxide of potassium.

Potassa, Potash, or Protoxide of Potassium, KO, is produced when potassium is heated in dry air: the metal burns, and becomes entirely converted into a volatile, fusible, white substance, which is anhydrous potassa. Moistened with water, it evolves great heat, and forms the hydrate.

The hydrate of potassa, KO, HO, is a very important substance, and one of great practical utility. It is always prepared for use by decomposing the carbonate by hydrate of lime, as in the following process, which is very convenient:—10 parts of carbonate of potassa are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or still better, silver vessel; 8 parts of good quicklime are meanwhile slaked in a covered basin, and the resulting hydrate of lime added, little by little, to the boiling solution of carbonate, with frequent stirring. When all the lime has been introduced, the mixture is suffered to boil a few minutes, and then removed from the fire, and covered up. In the course of a very short time, the solution will have become quite clear, and fit for decantation, the carbonate of lime, with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of carbonate of potassa be dilute, otherwise the decomposition becomes imperfect; the proportion of lime recommended is much greater than that required by theory, but it is always proper to have an excess.

The solution of hydrate, or, as it is commonly called, caustic potassa, may be concentrated by quick evaporation in the iron or silver vessel to any desired extent; when heated until vapour of water ceases to be disengaged, and then suffered to cool, it furnishes the solid hydrate, containing single equivalents of potassa and water.

Pure hydrate of potassa is a white solid substance, very deliquescent and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few of the compounds of this base; the solid hydrate of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline; it restores the blue colour to litmus which has been reddened by an acid; neutralizes completely the most powerful acids; has a naseous and peculiar taste, and dissolves the skin, and many other organic matters, when the latter are subjected to its action. It is constantly used by surgeons as a cautery, being moulded into little sticks for that purpose.

Hydrate of potassa, both in the solid state and in solution, rapidly absorbs carbonic acid from the air; hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it effervesces with an acid.

The water in this compound cannot be displaced by heat, the hydrate volatilizing as a whole at a very high temperature.

The following table of the densities and value in real alkali of different solutions of hydrate of potassa is given on the authority of Dr. Dalton.

Density.	Percentage of real alkali.	Density.	Percentage of real alkali.
1·68	51·2	1·33	26·3
1·60	46·7	1·28	23·4
1·52	42·9	1·23	19·5
1·47	39·6	1·19	16·2
1·44	36·8	1·15	13·0
1·42	34·4	1·11	9·5
1·39	32·4	1·06	4·7
1·36	29·4		

Teroxide of potassium, KO_3.—This is an orange-yellow fusible substance, generated when potassium is burned in excess of dry oxygen gas, and also formed, to a small extent, when hydrate of potassa is long exposed, in a melted state, to the air. When nitre is decomposed by a strong heat, peroxide of potassium is also produced. It is decomposed by water into potassa, which unites with the latter, and into oxygen gas.

Carbonate of potassa, KO, CO_2+2HO.—Salts of potassa containing a vegetable acid are of constant occurrence in plants, where they perform important, but not yet perfectly understood, functions in the economy of those beings. The potassa is derived from the soil, which, when capable of supporting vegetable life, always contains that substance. When plants are burned, the organic acids are destroyed, and the potassa left in the state of carbonate.

It is by these indirect means that carbonate, and, in fact, nearly all the salts of potassa, are obtained; the great natural depository of the alkali is the felspar of granitic and other unstratified rocks, where it is combined with silica, and in an insoluble state. Its extraction thence is attended with too many difficulties to be attempted on the large scale; but when these rocks disintegrate into soils, and the alkali acquires solubility, it is gradually taken up by plants, and accumulates in their substance in a condition highly favourable to its subsequent applications.

Potassa-salts are always most abundant in the green and tender parts of plants, as may be expected, since from these evaporation of nearly pure water takes place to a large extent; the solid timber of forest trees contains comparatively little.

In preparing the salt on an extensive scale, the ashes are subjected to a process called lixiviation; they are put into a large cask or tun, having an aperture near the bottom, stopped by a plug, and a quantity of water is added. After some hours the liquid is drawn off, and more water added, that the whole of the soluble matter may be removed. The weakest solutions are poured upon fresh quantities of ash, in place of water. The solutions are then evaporated to dryness, and the residue calcined, to remove a little brown organic matter; the product is the crude potash or pearlash of commerce, of which very large quantities are obtained from Russia and America. This salt is very impure; it contains silicate and sulphate of potassa, chloride of potassium, &c.

The purified carbonate of potassa of pharmacy is prepared from the crude article, by adding an equal weight of cold water, agitating, and filtering; most of the foreign salts are, from their inferior degree of solubility, left behind. The solution is then boiled down to a very small bulk, and suffered to cool, when the carbonate separates in small crystals containing 2 equiv. of water, which are drained from the mother-liquor, and then dried in a stove. A still purer salt may be obtained by exposing to a red-heat purified cream of tartar (acid tartrate of potassa), and separating the carbonate by solution in water and crystallization, or evaporation to dryness.

Carbonate of potassa is extremely deliquescent, and soluble in less than its own weight of water; the solution is highly alkaline to test-paper. It is insoluble in alcohol. By heat the water of crystallization is driven off, and by a temperature of full ignition the salt is fused, but not otherwise changed. This substance is largely used in the arts, and is a compound of great importance.

Bicarbonate of potassa, KO, CO_2+HO, CO_2.—When a stream of carbonic acid gas is passed through a cold solution of carbonate of potassa, the gas is rapidly absorbed, and a white, crystalline, and less soluble substance separated, which is the new compound. It is collected, pressed, re-dissolved in warm water, and the solution left to crystallize.

Bicarbonate of potassa is much less soluble than simple carbonate; it requires for that purpose 4 parts of cold water. The solution is nearly neutral to test-paper, and has a much milder taste than the preceding salt. When boiled, carbonic acid is disengaged. The crystals, which are large and beautiful, derive their form from a right rhombic prism; they are decomposed by heat, water and carbonic acid being extricated, and simple carbonate left behind.

NITRATE OF POTASSA; NITRE; SALTPETRE, KO, NO_5.—This important compound is a natural product, being disengaged by a kind of efflorescence from the surface of the soil in certain dry and hot countries. It may also be produced by artificial means, namely, by the oxidation of ammonia in presence of a powerful base.

In France, large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or hydrate of lime and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains nitrate of lime, mixed with carbonate of potassa; carbonate of lime is formed, and the nitric acid transferred to the alkali. The filtered solution is then made to crystallize, and the crystals purified by re-solution and crystallization several times repeated.

All the nitre used in this country comes from the East Indies; it is dissolved in water, a little carbonate of potassa added to precipitate lime, and then the salt purified as above.

Nitrate of potassa crystallizes in anhydrous six-sided prisms, with dihedral summits; it is soluble in 7 parts of water at 60° (15°·5C), and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colours. At a temperature below redness it melts, and by a strong heat is completely decomposed.

When thrown on the surface of many metals in a state of fusion, or when mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the nitric acid. Examples of such mixtures are found in common gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together nitrate of potassa, charcoal, and sulphur, in proportions which approach 1 eq. nitre, 3 eq. carbon, and 1 eq. sulphur.

These quantities give, reckoned to 100 parts, and compared with the proportions used in the manufacture of the English government powder,[1] the following results:—

	Theory.	Proportions in practice.
Nitrate of potassa	74·8	75
Charcoal	13·3	15
Sulphur	11·9	10
	100·	100

The nitre is rendered very pure by the means already mentioned, freed from water by fusion, and ground to fine powder: the sulphur and charcoal, the latter being made from light wood, as dogwood or elder, are also finely ground, after which the materials are weighed out, moistened with water, and thoroughly mixed, by grinding under an edge-mill. The mass is then subjected to great pressure, and the mill-cake thus produced broken in pieces,

[1] Dr. M'Culloch, Ency. Brit.

d placed in sieves made of perforated vellum, moved by machinery, each ntaining, in addition, a round piece of heavy wood. The grains of powder oken off by attrition fall through the holes in the skin, and are easily sepatad from the dust by sifting. The powder is, lastly, dried by exposure to eam-heat, and sometimes glazed or polished by agitation in a kind of cask ounted on an axis.

When gunpowder is fired, the oxygen of the nitrate of potassa is trans rred to the carbon, forming carbonic acid; the sulphur combines with the otassium, and the nitrogen is set free. The large volume of gas thus produced, and still farther expanded by the very exalted temperature, sufficiently accounts for the explosive effects.

SULPHATE OF POTASSA, KO,SO_3.—The acid residue left in the retort when itric acid is prepared is dissolved in water, and neutralized with crude carbonate of potassa. The solution furnishes, on cooling, hard transparent ystals of the neutral sulphate, which may be re-dissolved in boiling water, nd re-crystallized.

Sulphate of potassa is soluble in about 10 parts of cold, and in a much maller quantity of boiling water; it has a bitter taste, and is neutral to st-paper. The crystals much resemble those of quartz in figure and ap earance; they are anhydrous, and decrepitate when suddenly heated, hich is often the case with salts containing no water of crystallization. hey are quite insoluble in alcohol.

BISULPHATE OF POTASSA, $KO,SO_3 + HO,SO_3$. The neutral sulphate in owder is mixed with half its weight of oil of vitriol, and the whole evaporated quite to dryness in a platinum vessel, placed under a chimney; the esed salt is dissolved in hot water, and left to crystallize. The crystals ave the figure of flattened rhombic prisms, and are much more soluble than e neutral salt, requiring only twice their weight of water at 60° (15°·5C), d less than half that quantity at 212° (100°C). The solution has a sour ste and strong acid reaction.

BISULPHATE OF POTASSA, ANHYDROUS, $KO,2SO_3$.—Equal weights of neutral phate of potassa and oil of vitriol are dissolved in a small quantity of rm distilled water, and set aside to cool. The anhydrous sulphate crysllizes out in long delicate needles, which if left several days in the motheruor disappear, and give place to crystals of the ordinary hydrated bisulate above described. This salt is decomposed by a large quantity of ter.[1]

SESQUISULPHATE OF POTASSA, $2(KO,SO_3) + HO,SO_3$.—A salt, crytallizing fine needles resembling those of asbestos, and having the composition ted, was obtained by Mr. Phillips from the nitric acid residue. M. Jacquen was unsuccessful in his attempts to reproduce this compound.

CHLORATE OF POTASSA, KO,ClO_5.—The theory of the production of chloric d, by the action of chlorine gas on a solution of caustic potassa, has been eady described (p. 145).

Chlorine gas is conducted by a wide tube into a strong and warm solution carbonate of potassa, until absorption of the gas ceases. The liquid is, necessary, evaporated, and then allowed to cool, in order that the slightly uble chlorate may crystallize out. The mother-liquid affords a second p of crystals, but they are much more contaminated by chloride of potassm. It may be purified by one or two re-crystallizations.

Chlorate of potassa is soluble in about 20 parts of cold, and 2 of boiling ter; the crystals are anhydrous, flat, and tabular; in taste it somewhat embles nitre. Heated, it disengages oxygen gas from both acid and base, l leaves chloride of potassium. By arresting the decomposition when the

[1] *Jacquelain*, Ann. Chim. et Phys. vol. vii. p. 311.

evolution of gas begins, and re-dissolving the salt, perchlorate of potassa and chloride of potassium may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about one grain weight of chlorate and an equal quantity of sulphur are rubbed in a mortar, the mixture explodes with a loud report: hence it cannot be used in the preparation of gunpowder instead of nitrate of potassa. Chlorate of potassa is now a large article of commerce, being employed, together with phosphorus, in making instantaneous light matches.

Perchlorate of potassa. KO,ClO_7. — This has been already noticed under the head of perchloric acid. It is best prepared by projecting powdered chlorate of potassa into warm nitric acid, when the chloric acid is resolved into perchloric acid, chlorine, and oxygen gases. The salt is separated by crystallization from the nitrate. Perchlorate of potassa is a very feebly soluble salt: it requires 55 parts of cold water, but is more freely taken up at a boiling heat. The crystals are small, and have the figure of an octahedron, with square base. It is decomposed by heat, in the same manner as chlorate of potassa.

Sulphides of potassium. — There are not less than five or six distinct compounds of potassium and sulphur, of which, however, only three are of sufficient importance to be noticed here; these are the compounds, containing KS, KS_3, and KS_5.

Simple or protosulphide of potassium, is formed by directly combining the metal with sulphur, or by reducing sulphate of potassa at a red-heat by hydrogen or charcoal powder. Another method is to take a strong solution of hydrate of potassa, and after dividing it into two equal portions, saturate the one with sulphuretted hydrogen gas, and then add the remainder. The whole is then evaporated to dryness in a retort, and the residue fused.

The protosulphide is a crystalline cinnabar-red mass, very soluble in water. The solution has an exceedingly offensive and caustic taste, and is decomposed by acids, even carbonic acid, with evolution of sulphuretted hydrogen, and formation of a salt of the acid used. This compound is a strong sulphur-base, and unites with the sulphides of hydrogen, carbon, arsenic, &c., forming crystallizable saline compounds, One of these, KS+HS, is produced when hydrate of potassa is saturated with sulphuretted hydrogen, as before mentioned.

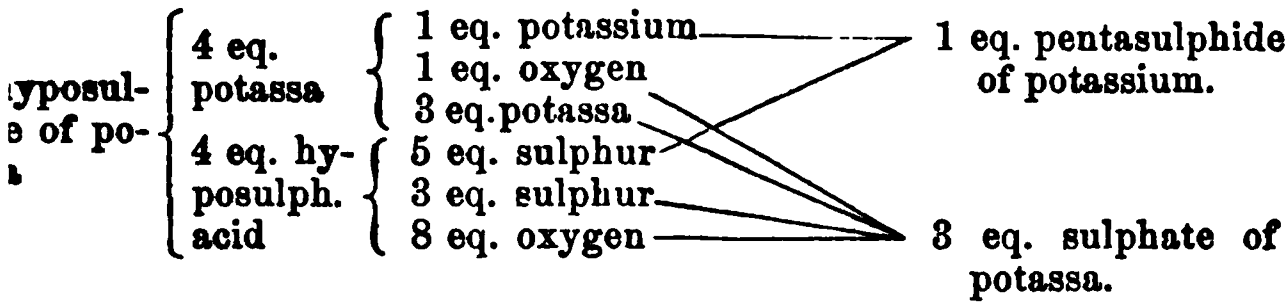
The higher sulphides are obtained by fusing the protosulphide with different proportions of sulphur. They are soluble in water, and decomposed by acids, in the same manner as the foregoing compound, with this addition, that the excess of sulphur is precipitated as a fine white powder.

Hepar sulphuris is a name given to a brownish substance, sometimes used in medicine, made by fusing together different proportions of carbonate of potassa and sulphur. It is a variable mixture of the two higher sulphides with hyposulphite and sulphate of potassa.

When equal parts of sulphur and dry carbonate of potassa are melted together at a temperature not exceeding 482° (250°C.), the decomposition of the salt is quite complete, and all the carbonic acid is expelled. The fused mass dissolves in water, with the exception of a little mechanically-mixed sulphur, with dark brown colour, and the solution is found to contain nothing besides pentasulphide of potassium and hyposulphite of potassa.

3 eq. potassa	2 eq. potassium	2 eq. of pentasulphide of potassium.
	2 eq. oxygen	
	1 eq. potassa	
12 eq. sulphur	10 eq. sulphur	
	2 eq. sulphur	1 eq. hyposulphite of potassa.

n the mixture has been exposed to a temperature approaching that tion, it is found on the contrary to contain sulphate of potassa, arising he decomposition of the hyposulphite which then occurs.



n both these mixtures the pentasulphide of potassium may be ex- l by alcohol, in which it dissolves.

n the carbonate is fused with half its weight of sulphur only, then the phide, KS_3, is produced instead of that above indicated; 3 eq. of po- and 8 eq. of sulphur containing the elements of 2 eq. sulphide and 1 posulphite.

effects described happen in the same manner when hydrate of potassa stituted for the carbonate; and also, when a solution of the hydrate is with sulphur, a mixture of sulphide and hyposulphite always results.

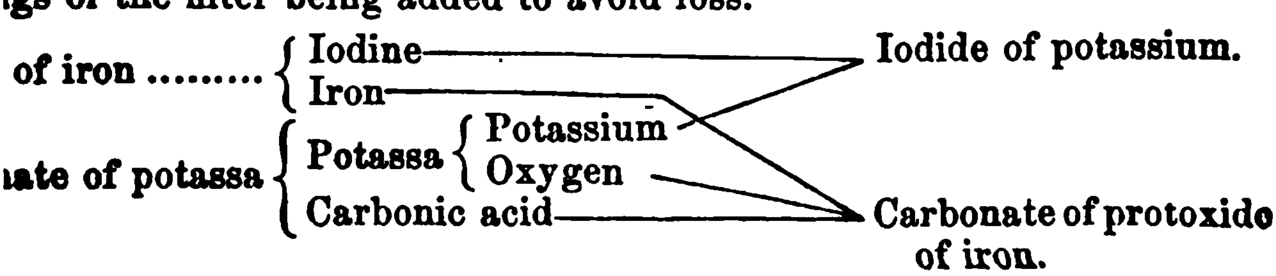
ORIDE OF POTASSIUM, KCl. — This salt is obtained in large quantity in nufacture of chlorate of potassa; it is easily purified from any portions latter by exposure to a dull red-heat. It is also contained in kelp, separated for the use of the alum-maker.

ride of potassium closely resembles common salt in appearance, as- , like that substance, the cubic form of crystallization. The crystals e in three parts of cold, and in a much less quantity of boiling water; re anhydrous, have a simple saline taste, with slight bitterness, and hen exposed to a red-heat. Chloride of potassium is volatilized by a igh temperature.

DE OF POTASSIUM, KI. — There are two different methods of preparing portant medicinal compound.

When iodine is added to a strong solution of caustic potassa free from ate, it is dissolved in large quantity, forming a colourless solution ning iodide of potassium and iodate of potassa; the reaction is the s in the analogous case with chlorine. When the solution begins to manently coloured by the iodine, it is evaporated to dryness, and cau- heated red-hot, by which the iodate of potassa is entirely converted dide of potassium. The mass is then dissolved in water, and after fil- , made to crystallize.

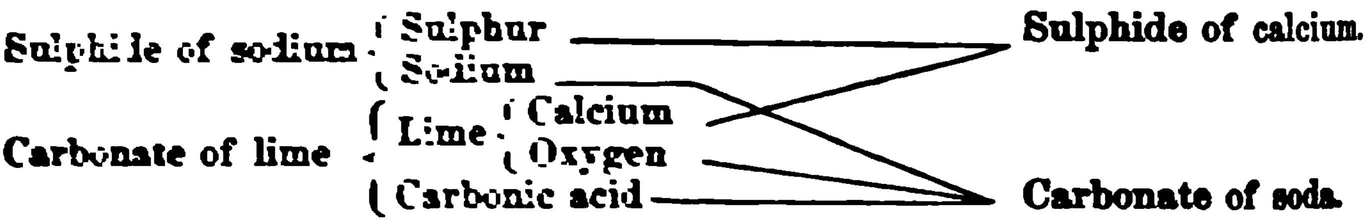
Iodine, water, and iron-filings or scraps of zinc, are placed in a warm on until the combination is complete, and the solution colourless. The ng iodide of iron or zinc is then filtered, and exactly decomposed with n of pure carbonate of potassa, great care being taken to avoid excess latter. Iodide of potassium and carbonate of protoxide of iron, or re obtained; the former is separated by filtration, and evaporated he solution is sufficiently concentrated to crystallize on cooling, the gs of the filter being added to avoid loss.



second method is, on the whole, to be preferred.

soda-ash in hot water, filtering the solution, and then allowing it to cool slowly, the carbonate is deposited in large transparent crystals.

The reaction which takes place in the calcination of the sulphate with chalk and coal-dust seems to consist, first, in the conversion of the sulphate of soda into sulphide of sodium by the aid of the combustible matter, and, secondly, in the double interchange of elements between that substance and the carbonate of lime.



The sulphide of calcium combines with another proportion of lime to form a peculiar compound, which is insoluble in cold or slightly warm water.

Other processes have been proposed, and even carried into execution, but the above, which was originally proposed by M. Leblanc, is found most advantageous.

The ordinary crystals of carbonate of soda contain ten equivalents of water, but by particular management the same salt may be had with fifteen, nine, seven, equivalents, or sometimes with only one. The common form of the crystal is derived from an oblique rhombic prism: they effloresce in dry air, and crumble to a white powder. Heated, they fuse in their water of crystallization: when the latter has been expelled, and the dry salt exposed to a full red-heat, it melts without undergoing change. The common crystals dissolve in two parts of cold, and in less than their own weight of boiling water: the solution has a strong, disagreeable, alkaline taste, and a powerful alkaline reaction.

Bicarbonate of soda, $NaO.CO_2 + HO.CO_2$. — This salt is prepared by passing carbonic acid gas into a cold solution of the neutral carbonate, or by placing the crystals in an atmosphere of the gas, which is rapidly absorbed, while the crystals lose the greater part of their water, and pass into the new compound.

Bicarbonate of soda, prepared by either process, is a crystalline white powder, which cannot be re-dissolved in warm water without partial decomposition. It requires 10 parts of water at 60° (15°·5C) for solution; the liquid is feebly alkaline to test-paper, and has a much milder taste than that of the simple carbonate. It does not precipitate a solution of magnesia. By exposure to heat, the salt is converted into neutral carbonate.

A sesquicarbonate of soda containing $2NaO.3CO_2 + 4HO$ has been described by Mr. Phillips; like the sesquicarbonate of potassa, it is formed at pleasure only with difficulty. This salt occurs native on the banks of the soda-lakes of Sokena in Africa, whence it is exported under the name of *trona*.

Alkalimetry; Analysis of Hydrates and Carbonates of the Alkalis. — The general principle of these operations consists in ascertaining the quantity of real alkali in a given weight of the substance examined, by finding how much of the latter is required to neutralize a known quantity of an acid, as sulphuric acid.

The first step is the preparation of a stock of dilute sulphuric acid of determinate strength; containing, for example, 100 grains of real acid in every 1,000 grain-measures of liquid:[1] a large quantity, as a gallon or more,

[1] The capacity of 1,000 grains of distilled water at 60° (15°5C). The grain-measure of water is often found a very convenient and useful unit of volume in chemical researches. Vessels graduated on this plan bear simple comparison with the imperial gallon and pint, and frequently also enable the operator to measure out a liquid of known density instead of weighing it.

ıy be prepared at once by the following means. The oil of vitriol is first amined; if it be good and of the sp. gr. 1·85 or near it, the process is exmely simple; every 49 grains of the liquid acid contains 40 grains of solute acid; the quantity of the latter required in the gallon, or 70,000 ain-measures of dilute acid, will be of course 7,000 grains. This is equi ılent to 8,571 grains of the oil of vitriol, for

Real acid.		Oil of vitriol.				
40	:	49	=	7000	:	8575

All that is required to be done, therefore, is to weigh out 8,575 grains of il of vitriol, and dilute it with so much water, *that the mixture, when cold, shall measure exactly one gallon.*

It very often happens, however, that the oil of vitriol to be used is not so strong as that above mentioned; in which case it is necessary to discover its real strength, as estimated from its saturating power. Pure anhydrous carbonate of soda is prepared by heating to dull redness, without fusion, the bicarbonate; of this salt 53 grains, or 1 eq., correspond to 31 grains of soda, and neutralize 40 grains of real sulphuric acid.

A convenient quantity is carefully weighed out, and added, little by little, to a known weight, say 100 grains, of the oil of vitriol to be tried, diluted with four or five times its weight of water, until the liquid, after warming, becomes quite neutral to test-paper. By weighing again the residue of the carbonate, it is at once known how much of the latter has been employed; the amount of real acid in the hundred parts of the oil of vitriol is then easily calculated. Thus, suppose the quantity of carbonate of soda used to be 105 grains; then,

Carb. soda.		Sulph. acid.				
53	:	40	=	105	:	79·24;

9·24 grains of real acid are consequently contained in 100 grains f oil of vitriol; consequently,

79·24	:	100	=	7000	:	8833·82

Fig. 146.

e weight in grains of the oil of vitriol required to make one allon of the dilute acid.

The "alkalimeter" is next to be constructed. This is merely a 000-grain measure, made of a piece of even, cylindrical glass tube, bout 15 inches long and 0·6 inch internal diameter, closed at one xtremity, and moulded into a spout or lip at the other. Fig. 146. strip of paper is pasted on the tube and suffered to dry, after hich the instrument is graduated by counterpoising it in a nearly pright position in the pan of a balance of moderate delicacy, and eighing into it, in succession, 100, 200, 300, &c., grains of distilled water at 60° (15°·5C), until the whole quantity, amounting 1,000 grains, has been introduced, the level of the water in the ibe being, after each addition, carefully marked with a pen upon e strip of paper, while the tube is held quite upright, and the ark made between the top and the bottom of the curve formed by e surface of the water. The smaller divisions of the scale, of 10 rains each, may then be made by dividing by compasses each of e spaces into ten equal parts. When the graduation is complete, d the operator is satisfied with its accuracy, the marks may be ansferred to the tube itself by a sharp file, and the paper removed y a little warm water. The numbers are scratched on the glass with the rd end of the same file, or with a diamond. When this alkalimeter is used

with the dilute acid described, every division of the glass will correspond to one grain of real sulphuric acid.

Let it be required, by way of example, to test the commercial value of soda-ash, or to examine it for scientific purposes: 50 grains of the sample are weighed out, dissolved in a little warm water, and, if necessary, the solution filtered: the alkalimeter is then filled to the top of the scale with the test-acid, and the latter poured from it into the alkaline solution, which is tried from time to time with red litmus-paper. The addition of acid must of course be made very cautiously as neutralization advances. When the solution, after being heated a few minutes, no longer affects either blue or red test-paper, the measure of liquid employed is read off, and the quantity of soda present in the state of carbonate or hydrate in the 50 grains of salt found by the rule of proportion. Suppose 33 measures, consequently 33 grains of acid, have been taken; then

Sulph. acid.		Soda.				
40	:	31	=	33	:	25·57;

the sample contains, therefore, 51·2 per cent. of available alkali.

It will be easily seen that the principle of the process described admits of very wide application, and that, by the aid of the alkalimeter and carefully prepared test-acid, the hydrates and carbonates of potassa, soda, and ammonia, both in the solid state and in solution, can be examined with great ease aud accuracy. The quantity of real alkali in a solution of caustic ammonia may thus be determined, the equivalent of that substance, and the amount of acid required to neutralize a known weight, being inserted as the second and third terms in the above rule-of-three statement. The same acid answers for all.

It is often desirable, in the analysis of carbonates, to determine directly the proportion of carbonic acid; the following methods leave nothing to be desired in point of precision: —

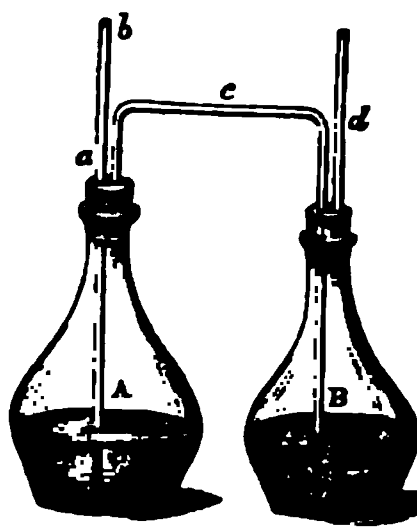
Fig. 147.

A small light glass flask (fig. 147) of three or four ounces capacity, with lipped edge, is chosen, and a cork fitted to it. A piece of tube about three inches long is drawn out at one extremity, and fitted by means of a small cork and a bit of bent tube, to the cork of the flask. This tube is filled with fragments of chloride of calcium, prevented from escaping by a little cotton at either end; the joints are secured by sealing-wax. A short tube, closed at one extremity, and small enough to go into the flask, is also provided, and the apparatus is complete. Fifty grains of the carbonate to be examined are carefully weighed out and introduced into the flask, together with a little water, the small tube is then filled with oil of vitriol, and placed in the flask in a nearly upright position, and leaning against its side in such a manner that the acid does not escape. The cork and chloride of calcium tube are then adjusted, and the whole apparatus accurately counterpoised on the balance. This done, the flask is slightly inclined, so that the oil of vitriol may slowly mix with the other substances and decompose the carbonate, the gas from which escapes in a dry state from the extremity of the tube. When the action has entirely ceased the liquid, is heated until it boils, and the steam begins to condense in the drying-tube; it is then left to cool, and weighed, when the loss indicates the quantity of carbonic acid. The acid must be in excess after the experiment. When carbonate of lime is thus analyzed, strong hydrochloric acid must be substituted for the oil of vitriol.

Instead of the above apparatus, a neat arrangement may be used which

first suggested by Will and Fresenius. It consists of two small glass ks, A and B, fig. 148, the latter being somewhat smaller than the former. th the flasks are provided with a doubly perforated cork. A tube, open at h ends, but closed at the upper extremity by means of a small quantity of x, passes through the cork of A. to the very ttom of the flask, whilst a second tube reaching to the bottom of B, establishes a communition between the two flasks. The cork of B provided, moreover, with a short tube, *d*. In der to analyse a carbonate, a suitable quany (fifty grains) is put into A, together with me water. B is half filled with concentrated lphuric acid, the apparatus tightly fitted and ighed. A small quantity of air is now cked out of flask B by means of the tube *d*, iereby the air in A is likewise rarified. Imediately a portion of sulphuric acid ascends the tube *c*, and flows over into flask A, using a disengagement of carbonic acid, hich escapes at *d*, after having been perfectly ied by passing through the bottle B. This eration is repeated until the whole of the carbonate is decomposed, and e process terminated by opening the wax stopper and drawing a quantity air through the apparatus. The apparatus is now re-weighed. The difrence of the two weighings expresses the quantity of carbonic acid in the mpound analysed.[1]

Fig. 148.



Sulphate of soda, Glauber's salts, $NaO, SO_3 + 10HO$. — This is a byoduct in several chemical operations; it may of course be prepared rectly, if wanted pure, by adding dilute sulphuric acid to saturation to a lution of carbonate of soda. It crystallizes in a figure derived from an lique rhombic prism; the crystals contain 10 eq. of water, are efflorest, and undergo watery fusion when heated, like those of the carbonate; ey are soluble in twice their weight of cold water, and rapidly increase in lubility as the temperature of the liquid rises to 91°·5 (33°C), when a aximum is reached, 100 parts of water dissolving 322 parts of the salt. eated beyond this point, the solubility diminishes, and a portion of sulate is deposited. A warm saturated solution, evaporated at a high tempeture, deposits opaque prismatic crystals, which are anhydrous. This salt s a slightly bitter taste, and is purgative. Mineral springs sometimes conin it, as at Cheltenham.

Bisulphate of soda, $NaO,SO_3 + HO,SO_3 + 3HO$.—This is prepared by lding to 10 parts of anhydrous neutral sulphate, 7 of oil of vitriol, evapoting the whole to dryness, and gently igniting. The bisulphate is very luble in water, and has an acid reaction. It is not deliquescent. When ry strongly heated, the fused salt gives up anhydrous sulphuric acid, and comes simple sulphate; a change which necessarily supposes the previous rmation of a true anhydrous bisulphate, $NaO,2SO_3$.

Hyposulphite of soda, NaO, S_2O_2. — There are several modes of procung this salt, which is now used in considerable quantity for photographic rposes. One of the best is to form neutral *sulphite* of soda, by passing a ream of well washed sulphurous acid gas into a strong solution of carbote of soda, and then to digest the solution with sulphur at a gentle heat ring several days. By careful evaporation at a modern temperature, the lt is obtained in large and regular crystals, which are very soluble in water.

[1] *A convenient modification of this has been made by* Dr. Wetherill, (Journ. Frank. Inst.) *another by Schaffner.* (Chem. Gazette, Jan. 15, 1853.—R. B.)

NITRATE OF SODA; CUBIC NITRE, NaO, NO_5.—Nitrate of soda occurs native, and in enormous quantity, at Atacama, in Peru, where it forms a regular bed, of great extent, covered with clay and alluvial matter. The pure salt commonly crystallizes in rhombohedrons, resembling those of calcareous spar, but is probably dimorphous. It is deliquescent, and very soluble in water. Nitrate of soda is employed for making nitric acid, but cannot be used for gunpowder, as the mixture burns too slowly, and becomes damp in the air. It has been lately used with some success in agriculture as a superficial manure or top-dressing.

PHOSPHATES OF SODA; COMMON TRIBASIC PHOSPHATE, $2NaO, HO, PO_5+24HO$.—This beautiful salt is prepared by precipitating the acid phosphate of lime obtained by decomposing bone-earth by sulphuric acid, with a slight excess of carbonate of soda. It crystallizes in oblique rhombic prisms, which are efflorescent. The crystals dissolve in 4 parts of cold water, and undergo the aqueous fusion when heated. The salt is bitter and purgative; its solution is alkaline to test-paper. Crystals containing 14 equivalents of water, and having a form different from that above mentioned, have been obtained.

A second tribasic phosphate, sometimes called subphosphate, $3NaO, PO_5+24HO$, is obtained by adding a solution of caustic soda to the preceding salt. The crystals are slender six-sided prisms, soluble in 5 parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat, except the loss of its water of crystallization. Its solution is strongly alkaline. A third tribasic phosphate, often called superphosphate or biphosphate, $NaO,2HO,PO_5+2HO$, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate chloride of barium, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, the salt becomes changed into monobasic phosphate of soda.

Tribasic phosphate of soda, ammonia, and water; microcosmic salt, NaO, NH_4O,HO,PO_5+8HO. — Six parts of common phosphate of soda are heated with 2 of water until the whole is liquefied, when 1 part of powdered sal-ammoniac is added; common salt separates, and may be removed by a filter, and from the solution, duly concentrated, the new salt is deposited in prismatic crystals, which may be purified by one or two re-crystallizations. Microcosmic salt is very soluble. When gently heated, it parts with the 8 eq. of water crystallization, and, at a higher temperature, the water acting as base is expelled, together with the ammonia, and a very fusible compound, metaphosphate of soda, remains, which is valuable as a flux in blowpipe experiments. This salt is said to occur in the urine.

BIBASIC PHOSPHATE OF SODA; PYROPHOSPHATE OF SODA, $2\,NaO,PO_5+10HO$. — Prepared by strongly heating common phosphate of soda, dissolving the residue in water, and re-crystallizing. The crystals are very brilliant, permanent in the air, and less soluble than the original phosphate; their solution is alkaline. A bibasic phosphate, containing an equivalent of basic water, has been obtained; it does not, however, crystallize.

MONOBASIC PHOSPHATE OF SODA; METAPHOSPHATE OF SODA, NaO,PO_5.—Obtained by heating either the acid tribasic phosphate, or microcosmic salt. It is a transparent glassy substance, fusible at a dull red-heat, deliquescent, and very soluble in water. It refuses to crystallize, but dries up into a gum-like mass.

If this glassy phosphate be cooled very slowly a beautifully crystalline mass is obtained. It may be separated by means of boiling water from the vitreous metaphosphate which will not crystallize. Another metaphosphate has been obtained by adding sulphate of soda to an excess of phosphoric acid, *evaporating* and heating to upwards of 600° (315°·5C). Possibly these

several metamosphates may be represented by the formulæ NaO,PO_5; $2NaO,2PO_5$; $3NaO,3PO_5$.

The tribasic phosphates give a bright yellow precipitate with solution of nitrate of silver; the bibasic and monobasic phosphates afford white precipitates with the same substance. The salts of the two latter classes, fused with excess of carbonate of soda, yield the tribasic modification of the acid.

Phosphates intermediate between the monobasic and bibasic phosphates of soda, $3NaO,2PO_5$, and $6NaO,5PO_5$. — The first is produced by fusing 100 parts of anhydrous pyrophosphate of soda, and 76·87 parts of metaphosphate of soda. The white crystalline mass is reduced to powder, and quickly exhausted with water. The solution, on exposure to the atmosphere, yields small plates which are very soluble in water.

The second is produced by fusing 100 parts of pyrophosphate of soda, and 307·5 of metaphosphate; it crystallizes with more difficulty than the preceding compound.

MM. Fleitmann and Henneberg, the discoverers of these new phosphates, represent the different phosphates thus: —

Common phosphate	$6NaO,2PO_5$
Pyrophosphate	$6NaO,3PO_5$
New phosphates	$6NaO,4PO_5$ $6NaO,5PO_5$
Metaphosphate	$6NaO,6PO_5$

In each of which six equivalents of the base are combined with a different polymeric acid.

Biborate of soda; borax, $NaO,2BO_3+10HO$. —This compound occurs in the waters of certain lakes in Thibet and Persia; it is imported in a crude state from the East Indies under the name of *tincal*. When purified, it constitutes the borax of commerce. Much borax is now, however, manufactured from the native boracic acid of Tuscany. Borax crystallizes in six-sided prisms, which effloresce in dry air, and require 20 parts of cold, and ·6 of boiling water for solution. Exposed to heat, the 10 eq. of water of crystallization are expelled, and at a higher temperature the salt fuses, and assumes a glassy appearance on cooling; in this state it is much used for blowpipe experiments, the metallic oxides dissolving in it to transparent beads, many of which are distinguished by characteristic colours. By particular management, crystals of borax can be obtained with 5 eq. of water; they are very hard, and permanent in the air. Although by constitution an acid salt, borax has an alkaline reaction to test-paper. It is used in the arts for soldering metals, its action consisting in rendering the surfaces to be joinea metallic, by dissolving the oxides, and sometimes enters into the composition of the glaze with which stoneware is covered.

Neutral borate of soda may be formed by fusing together borax and carbonate of soda in equivalent proportions, and then dissolving the mass in water. The crystals are large, and contain NaO,BO_3+8HO.

Sulphide of sodium, NaS. — Prepared in the same manner as the protosulphide of potassium; it separates from a concentrated solution in octahedral crystals, which are rapidly decomposed by contact of air into a mixture of hydrate and hyposulphite of soda. It forms double sulphur-salts with sulphuretted hydrogen, bisulphide of carbon, and other sulphur-acids.

Sulphide of sodium is supposed to enter into the composition of the beautiful pigment *ultramarine*, prepared from the *lapis lazuli*, and which is now imitated by artificial means.[1]

Chloride of sodium; common salt, NaCl. — This very important sub-

[1] See Pharmaceutical Journal, ii. 53.

stance is found in many parts of the world in solid beds or irregular strata of immense thickness, as in Cheshire, for example, in Spain, Galicia, and many other localities. An inexhaustible supply exists also in the waters of the ocean, and large quantities are annually obtained from saline springs.

The rock-salt is almost always too impure for use; if no natural brine-spring exist, an artificial one is formed by sinking a shaft into the rock-salt, and, if necessary, introducing water. This, when saturated, is pumped up, and evaporated more or less rapidly in large iron pans. As the salt separates, it is removed from the bottom of the vessels by means of a scoop, pressed while still moist into moulds, and then transferred to the drying-stove. When large crystals are required, as for the coarse-grained *bay-salt* used in curing provisions, the evaporation is slowly conducted. Common salt is apt to be contaminated with chloride of magnesium.

When pure, this substance is not deliquescent in moderately dry air. It crystallizes in anhydrous cubes, which are often grouped together into pyramids, or steps. It requires about 2½ parts of water at 60° (15°·5C) for solution, and its solubility is not sensibly increased by heat; it dissolves to some extent in spirits, but is nearly insoluble in absolute alcohol. Chloride of sodium fuses at a red-heat, and is volatile at a still higher temperature. The economical uses of common salt are well known.

The *iodide* and *bromide of sodium* much resemble the corresponding potassium-compounds: they crystallize in cubes which are anhydrous, and are very soluble in water.

There is no good precipitant for soda, all the salts being very soluble with the exception of antimonate of soda, the use of which is attended with difficulties; its presence is often determined by purely negative evidence. The yellow colour imparted by soda-salt to the outer flame of the blowpipe, and to combustible matter, is a character of some importance.

AMMONIUM.

In connection with the compounds of potassium and sodium, those formed by ammonia are most conveniently studied. Ammoniacal salts correspond in every respect in constitution with those of potassa and soda; in all cases the substance which replaces those alkalis is hydrate of ammonia, or, as it is now almost generally considered, the oxide of a hypothetical substance called ammonium, capable of playing the part of a metal, and ismorphous with potassium and sodium. All attempts to isolate this substance have failed, apparently from its tendency to separate into ammonia and hydrogen gas.

When a globule of mercury is placed on a piece of moistened caustic potassa, and connected with the negative side of a voltaic battery of very moderate power, while the circuit is completed through the platinum plate upon which rests the alkali, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed.

If this experiment be now repeated with a piece of sal-ammoniac instead of hydrate of potassa, a soft solid, metalline mass is also produced, which has been called the *ammoniacal amalgam*, and considered to contain ammonium in combination with mercury. A still simpler method of preparing this extraordinary compound is the following:—A little mercury is put into a test-tube with a grain or two of potassium or sodium, and gentle heat applied; combination ensues, attended by heat and light. When cold, the fluid amalgam is put into a capsule, and covered with a strong solution of sal-ammoniac. The production of ammoniacal amalgam instantly commences, the mercury increases prodigiously in volume, and becomes quite

y. The increase of weight is, however, quite trifling; it varies from ,th to $\frac{1}{12000}$th part.

eft to itself, the amalgam quickly decomposes into fluid mercury, ammo- and hydrogen.

; is difficult to offer any opinion concerning the real nature of this com- nd: something analogous occurs when pure silver is exposed to a very ı temperature, much above its melting-point, in contact with air or oxy- gas; the latter is absorbed in very large quantity, amounting, accord- to the observation of Gay-Lussac, to 20 times the volume of the silver, is again disengaged on lessening the heat. The metal loses none of its re, and is not sensibly altered in other respects.

he great argument in favour of the existence of ammonium is founded the perfect comparison which the ammoniacal salts bear with those of alkaline metals.

he equivalent of ammonium is 18; its symbol is NH_4.

HLORIDE OF AMMONIUM; (MURIATE OF AMMONIA;) SAL-AMMONIAC, NH_4Cl. al-ammoniac was formerly obtained from Egypt, being extracted by sub- ation from the soot of camels' dung; it is now largely manufactured from ammoniacal liquid of the gas-works, and from the condensed products he distillation of bones, and other animal refuse, in the preparation of nal charcoal.

'hese impure and highly offensive solutions are treated with slight excess ıydrochloric acid, by which the alkali is neutralized, and the carbonate sulphide decomposed with evolution of carbonic acid and sulphuretted rogen gases. The liquid is evaporated to dryness, and the salt carefully ted, to expel or decompose the tarry matter; it is then purified by sub- ation in large iron vessels lined with clay, surmounted with domes of lead. ublimed sal-ammoniac has a fibrous texture, it is tough, and difficult to rder.

/hen crystallized from water it separates under favourable circumstances, listinct cubes or octahedrons; but the crystals are usually small, and ag- gated together in rays. It has a sharp saline taste, and is soluble in $2\frac{3}{4}$ ts of cold, in a much smaller quantity of hot water. By heat, it is sub- ed without decomposition. The crystals are anhydrous. Chloride of nonium forms double salts with chloride of magnesium, nickel, cobalt, ıganese, zinc, and copper.

SULPHATE OF OXIDE OF AMMONIUM; SULPHATE OF AMMONIA, NH_4O, $+HO$. — Prepared by neutralizing carbonate of ammonia by sulphuric l, or on a large scale, by adding sulphuric acid in excess to the coal-gas or just mentioned, and purifying the product by suitable means. It is ıble in 2 parts of cold water, and crystallizes in long, flattened, six-sided ms, which lose an equivalent of water when heated. It is entirely de- posed, and driven off by ignition, and, even to a certain extent, by long ing with water, ammonia being expelled and the liquid rendered acid.

CARBONATES OF AMMONIA. — These compounds have been carefully exam- l by Professor Rose, of Berlin,[1] and appear very numerous. The *neutral, ydrous carbonate*, NH_3,CO_2, is prepared by the direct union of carbonic l with ammoniacal gas, both being carefully cooled. The gases combine he proportions of one measure of the first to two of the second, and give to a pungent, and very volatile compound, which condenses in white ks. It is very soluble in water. The pungent, transparent, carbonate ımmonia of pharmacy, which is prepared by subliming a mixture of sal- noniac and chalk, always contains less base than that required to form utral carbonate. Its composition varies a good deal, but in freshly pre-

[1] *Annalen der Pharmacie*, xxx. 45

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pared specimens approaches that of a sesquicarbonate of oxide of ammonium, $2\ NH_4O,3CO_2$.—When heated in a retort, the neck of which dips into mercury, it is decomposed, with disengagement of pure carbonic acid, into neutral hydrated carbonate of ammonia, and several other compounds. Exposed to the air at common temperatures, it disengages neutral carbonate of ammonia, loses its pungency, and crumbles down to a soft, white powder, which is a bicarbonate, containing NH_4O,CO_2+HO,CO_2. This is a permanent combination, although still volatile. When a strong solution of the commercial sesquicarbonate is made with tepid water, and filtered, warm, into a close vessel, large and regular crystals of bicarbonate, having the above composition, are sometimes deposited after a few days. These are inodorous, quite permanent in the air, and resemble, in the closest manner, crystals of bicarbonate of potassa.

Nitrate of Oxide of Ammonium; nitrate of ammonia, NH_4O,NO_5.—Easily prepared by adding carbonate of ammonia to slightly diluted nitric acid until neutralization has been reached. By slow evaporation at a moderate temperature it crystallizes in six-sided prisms, like those of nitrate of potassa; but, as usually prepared for making nitrous oxide, by quick boiling, until a portion solidifies completely on cooling, it forms a fibrous and indistinct crystalline mass.

Nitrate of ammonia dissolves in 2 parts of cold water, is but feebly deliquescent, and deflagrates like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained.[1]

Sulphides of Ammonium.—Several of these compounds exist, and may be formed by distilling with sal-ammoniac the corresponding sulphides of potassium or sodium.

The *double sulphide of ammonium and hydrogen*, NH_4S+HS, commonly called hydrosulphate of ammonia, or, more correctly, hydrosulphate of sulphide of ammonium, is a compound of great practical utility; it is obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until no more of the latter is absorbed. The solution is nearly colourless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.[2]

When dry ammoniacal gas is brought in contact with anhydrous sulphuric acid, a white crystalline compound is produced, which is soluble in water. In a freshly prepared cold solution of this substance neither sulphuric acid nor ammonia can be found; but after standing some time, and especially if heat be applied, it passes into ordinary sulphate of ammonia.

A compound of dry ammoniacal gas and sulphurous acid also exists; it is a yellow soluble substance, altogether distinct from sulphite of ammonia.

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[1] Page 125.

[2] Phosphates of Oxide of Ammonium; Common Tribasic Phosphate, $2\ NH_4O,HO,PO_5+HO$.—This salt is formed by precipitating the acid phosphate of lime with an excess of carbonate of ammonia. The solution is allowed to evaporate spontaneously or by a gentle heat. In the latter case ammonia is lost and it becomes necessary to saturate the acid set free, previous to crystallization. It crystallizes in six-sided tables derived from oblique quadrangular prisms. Its crystals are efflorescent, soluble in alcohol, and soluble in four times its weight of cold water. Its solution has an alkaline, slightly saline taste and alkaline reaction. By heat ammonia is disengaged.

The acid tribasic phosphate, $NH_4O.2HO.PO_5+4HO$, is formed when a solution of the common phosphate is boiled as long as ammonia is given off. It crystallizes in four-sided prisms. Its crystals are permanent, soluble in 5 parts of cold water, acid in taste and reaction.

Another tribasic phosphate, $3NH_4O.PO_5$ subphosphate is formed by adding ammonia to either of the above It falls as a slightly soluble granular precipitate.—R. B.

ry carbonic acid and ammonia also unite to form a volatile white powder, s already mentioned.

When certain salts, especially chlorides in an anhydrous state, are exposed ammoniacal gas, the latter is absorbed with great energy, and the combinations formed are not always easily decomposed by heat. The chlorides of opper and silver absorb, in this manner, large quantities of the gas. All hese compounds must be carefully distinguished from the true ammoniacal alts containing ammonium or its oxide.

There is supposed to be yet another compound of hydrogen and nitrogen which the term *amidogen* has been given. When potassium is heated in he vapour of water, this substance is decomposed, hydrogen is evolved, and he metal converted into oxide. When the same experiment is made with ry ammoniacal gas, hydrogen is also set free, and an olive-green crystalline ompound produced, supposed to contain potassium in union with a new body, NH_2, having an equivalent of hydrogen less than ammonia.

When ammonia is added to a solution of corrosive sublimate, a white precipitate is obtained, which has been long known in pharmacy. Sir R. Kane nfers, from his experiments, that this substance should be looked upon as a ompound of chloride of mercury with amide of mercury. The latter salt as not been obtained separately; still less has amidogen itself been isolated.

It has been thought that ammonia may be considered an amide of hydrogen, nalogous to water or oxide of hydrogen, capable of entering into combination with salts, and other substances, in a similar manner, yielding unstable nd easily decomposed compounds, which offer a great contrast to those of he energetic *quasi*-metal ammonium; the views of chemists upon this subject are, however, still divided.

The ammoniacal salts are easily recognised; they are all decomposed or olatilized by a high temperature; and when heated with hydrate of lime, r solution of alkaline carbonate, evolve ammonia, which may be known by ts odour and alkaline reaction. The salts are all more or less soluble, the cid tartrate of ammonia and the double chloride of ammonium and platinum eing among the least so; hence the salts of ammonia cannot be distinguished rom those of potassa by the tests of tartaric acid and platinum-solution.

LITHIUM.

A connecting link between this class of metals and the next succeeding. ithium is obtained by electrolyzing, in contact with mercury, the hydrate f lithia, and then decomposing the amalgam by distillation. It is a white etal like sodium, and very oxidable. The equivalent of lithium is 6·5, and s symbol L.

The oxide, lithia, LO, is found in petalite, spodumene, lepidolite, and a w other minerals, and sometimes occurs in minute quantities in mineral prings. From petalite it may be obtained, on the small scale, by the following process: — The mineral is reduced to an exceedingly fine powder, ixed with five or six times its weight of pure carbonate of lime, and the ixture heated to whiteness, in a platinum crucible, placed within a well-overed earthen one, for twenty minutes or half an hour. The shrunken oherent mass is digested in dilute hydrochloric acid, the whole evaporated dryness, acidulated water added, and the silica separated by a filter. The olution is then mixed with carbonate of ammonia in excess, boiled and ltered; the clear liquid is evaporated to dryness, and gently heated in a

platinum crucible, to expel the sal-ammoniac. The residue is then wetted with oil of vitriol, gently evaporated once more to dryness, and ignited; pure fused sulphate of lithia remains.

This process will serve to give a good idea of the general nature of the operation by which alkalis are extracted in mineral analysis, and their quantities determined.

The hydrate of lithia is much less soluble in water than those of potassa and soda; the carbonate and phosphate are also sparingly soluble salts. The chloride crystallizes in anhydrous cubes which are deliquescent. Sulphate of lithia is a very beautiful salt; it crystallizes in lengthened prisms containing one equivalent of water. It gives no double salt with sulphate of alumina.

The salts of lithia colour the outer flame of the blowpipe carmine-red.

SECTION II.

METALS OF THE ALKALINE EARTHS.

BARIUM.

[Bar]ium was obtained by Sir H. Davy by means similar to those mentioned [in the] case of lithium; it is procured more advantageously, by strongly heat[ing ba]ryta in an iron tube, through which the vapour of potassium is con[ducted]. The reduced barium is extracted by quicksilver, and the amalgam [distille]d in a small green glass retort.

[Bari]um is a white metal, having the colour and lustre of silver; it is mal[leable,] melts below a red heat, decomposes water, and gradually oxidizes in [the air].

[The] equivalent of this metal has been fixed at 68·5; its symbol is Ba.

[P]ROTOXIDE OF BARIUM; BARYTA, BaO. — Baryta,[1] or barytes, occurs in [nature] in considerable abundance as carbonate and sulphate, forming the [gangu]e in many lead-mines; from both these sources it may be extracted [with f]acility. The best method of preparing pure baryta is to decompose [the cr]ystallized nitrate by heat in a capacious crucible of porcelain until red [fume]s are no longer disengaged; the nitric acid is resolved into nitrous [acid a]nd oxygen, and the baryta remains behind in the form of a greyish [spong]y mass, fusible at a high degree of heat. When moistened with water, [it com]bines to a hydrate with great elevation of temperature.

[The] hydrate is a white, soft powder, having a great attraction for carbonic [acid, a]nd soluble in 20 parts of cold and 2 of boiling water; a hot saturated [solutio]n deposits crystals on cooling, which contain BaO, HO+9HO. Solu[tion o]f hydrate of baryta is a valuable re-agent; it is highly alkaline to [test-pa]per, and instantly rendered turbid by the smallest trace of carbonic [acid].

[BIN]OXIDE OF BARIUM, BaO_2. — This may be formed, as already mentioned, [by ex]posing baryta, heated to full redness in a porcelain tube, to a current [of pur]e oxygen gas. The binoxide is grey, and forms a white hydrate with [water,] which is not decomposed by that liquid in the cold, but dissolves in [small] quantity. The binoxide may also be made by heating pure baryta to [rednes]s in a platinum crucible, and then gradually adding an equal weight [of chl]orate of potassa; binoxide of barium and chloride of potassium are [form]ed. The latter may be extracted by cold water, and the binoxide [left in] the state of hydrate. It is interesting chiefly in its relation to bin[oxide] of hydrogen. When dissolved in dilute acid, it is decomposed by [chro]mate of potassa, oxide of silver, chloride of silver, sulphate and car[bonate] of silver.

[CHL]ORIDE OF BARIUM, BaCl+2HO. — This valuable salt is prepared by [dissolv]ing the native carbonate in hydrochloric acid, filtering the solution,

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[1] [Fro]m βαρύς, heavy, in allusion to the great specific gravity of the native carbonate and [sulphat]e.

and evaporating until a skin begins to form at the surface; the solution on cooling deposits crystals. When native carbonate cannot be procured, the native sulphate may be employed in the following manner:—The sulphate is reduced to fine powder, and intimately mixed with one-third of its weight of powdered coal; the mixture is pressed into an earthen crucible to which a cover is fitted, and exposed for an hour or more to a high red-heat, by which the sulphate is converted into sulphide at the expense of the combustible matter of the coal. The black mass obtained is powdered and boiled in water, by which the sulphide is dissolved; the solution is filtered hot, and mixed with a slight excess of hydrochloric acid; chloride of barium and sulphuretted hydrogen are produced; the latter escaping with effervescence. Lastly, the solution is filtered to separate any little insoluble matter, and evaporated to the crystallizing point.

The crystals of chloride of barium are flat, four-sided tables, colourless and transparent. They contain 2 equivalents of water, easily driven off by heat: 100 parts of water dissolve 43·5 parts at 60° (15°·5C), and 78 parts at 223° (106°·5C), which is the boiling-point of the saturated solution.

Nitrate of baryta, BaO, NO_5.—The nitrate is prepared by methods exactly similar to the above, nitric acid being substituted for the hydrochloric. It crystallizes in transparent colourless octahedrons, which are anhydrous. They require for solution 8 parts of cold, and 3 parts of boiling water. This salt is much less soluble in dilute nitric acid than in pure water; errors sometimes arise from such a precipitate of crystalline nitrate of baryta being mistaken for sulphate. It disappears on heating, or by large affusion of water.

Sulphate of baryta; heavy-spar; BaO,SO_3.—Found native, often beautifully crystallized. This compound is always produced when sulphuric acid or a soluble sulphate is mixed with a solution of a barytic salt. It is not sensibly soluble in water or in any dilute acid, even nitric; hot oil of vitriol dissolves a little, but the greater part separates again on cooling. Sulphate of baryta is used as a pigment, but often for the purpose of adulterating white-lead; the native salt is ground to fine powder and washed with dilute sulphuric acid, by which its colour is improved, and a little oxide of iron probably dissolved out. The specific gravity of the natural sulphate is as high as 4·4 to 4·8.

Sulphide of barium, BaS.—The protosulphide of barium is obtained in the manner already described; the higher sulphides may be formed by boiling this compound with sulphur. Protosulphide of barium crystallizes in thin and nearly colourless plates from a hot solution, which contain water, and are not very soluble; they are rapidly altered by the air. A strong solution of sulphide may be employed in the preparation of hydrate of baryta, by boiling it with small successive portions of black oxide of copper, until a drop of the liquid ceases to precipitate a salt of the lead black; the liquid being filtered, yields, on cooling, crystals of hydrate. In this reaction, besides hydrate of baryta, hyposulphite of that base, and sulphide of copper are produced; the latter is insoluble, and is removed by the filter, while most of the hyposulphite remains in the mother-liquor.

Carbonate of baryta, BaO, CO_2.—The natural carbonate is called *witherite;* the artificial is formed by precipitating the chloride or nitrate with an alkaline carbonate, or carbonate of ammonia. It is a heavy, white powder, very sparingly soluble in water, and chiefly useful in the preparation of the rarer baryta-salts.

Solutions of hydrate and nitrate of baryta and of the chloride of barium *are constantly* kept in the laboratory as chemical tests, the first being em-

loyed to effect the separation of carbonic acid from certain gaseous mixtures, and the two latter to precipitate sulphuric acid from solution.

The soluble salts of baryta are poisonous, which is not the case with those of the base next to be described.

STRONTIUM.

The metal strontium may be obtained from its oxide by means similar to those described in the case of barium; it is a white metal, heavy, oxidizable in the air, and capable of decomposing water at common temperatures.

The equivalent of strontium is 43·8, and its symbol is Sr.

Protoxide of strontium; strontia; SrO.—This compound is best prepared by decomposing the nitrate by the aid of heat; it resembles in almost every particular the earth baryta, forming, like that substance, a white hydrate, soluble in water. A hot saturated solution deposits crystals on cooling, which contain 10 equivalents of water. The hydrate has a great attraction for carbonic acid.

Binoxide of strontium, SrO_2.—The binoxide is prepared in the same manner as binoxide of barium; it may be substituted for the latter in making binoxide of hydrogen.

The native carbonate and sulphate of strontia, met with in lead-mines and other localities, serve for the preparation of the various salts by means exactly similar to those already described in the case of baryta; they have a very feeble degree of solubility in water.

Chloride of strontium, $SrCl$.—The chloride crystallizes in colourless needles or prisms, which are slightly deliquescent, and soluble in 2 parts of cold and still less of boiling water; they are also soluble in alcohol, and the solution, when kindled, burns with a crimson flame. The crystals contain 6 equivalents of water, which they lose by heat; at a higher temperature the chloride fuses.

Nitrate of strontia, SrO,NO_5.—This salt crystallizes in anhydrous octahedrons, which require for solution 5 parts of cold, and about half their weight of boiling water. It is principally of value to the pyrotechnist, who employs it in the composition of the well-known "red-fire."[1]

CALCIUM.

This is a silver-white and extremely oxidable metal, obtained with great difficulty by means analogous to those by which barium and strontium are procured.

The equivalent of calcium is 20; its symbol is Ca.

Protoxide of calcium; lime; CaO.—This extremely important compound may be obtained in a state of considerable purity by heating to full redness, for some time, fragments of the black bituminous marble of Derbyshire or Kilkenny. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial carbonate of lime, procured by precipitating the nitrate by carbonate of ammonia. Lime in an impure state is prepared for building and agricultural purposes by calcining

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[1] **Red-Fire:—**

	Grns.
Dry nitrate of strontia	800
Sulphur	225
Chlorate of potassa	200
Lampblack	50

Green-Fire:—

	Grns.
Dry nitrate of baryta	450
Sulphur	150
Chlorate of potassa	100
Lampblack	25

The strontia or baryta-salt, the sulphur, and the lampblack, must be finely powdered and intimately mixed, after which *the chlorate of* potassa should be added in rather coarse powder, and mixed *without much rubbing* with the other ingredients. The red-fire composition *has been known to ignite spontaneously*.

in a kiln of suitable construction, the ordinary limestones which abound in many districts; a red-heat, continued for some hours, is sufficient to disengage the whole of the carbonic acid. In the best contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestones contain silica, and the heat has been very high, the lime refuses to slake, and is said to be *over-burned;* in this case a portion of silicate has been formed.

Pure lime is white, and often of considerable hardness; it is quite infusible, and phosphoresces, or emits a pale light at a high temperature. When moistened with water, it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single equivalent of water; the latter can be again expelled by a red-heat. This hydrate is soluble in water, but far less so than either the hydrate of baryta or of strontia, and what is very remarkable, the *colder* the water, the larger the quantity of the compound which is taken up. A pint of water at 60° (15°·5C) dissolves about 11 grains, while at 212° (100°C) only 7 grains are retained in solution. The hydrate has been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating cold water with excess of hydrate of lime in a closely-stopped vessel, and then, after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another occasion;—there is not the least occasion for filtering the solution. Lime-water has a strong alkaline reaction, a nauseous taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid from the atmosphere. It is used, like baryta-water, as a test for that substance, and also in medicine. Lime-water prepared from some varieties of limestone may contain potassa.

The hardening of mortars and cements is in a great measure due to the gradual absorption of carbonic acid; but even after a very great length of time, this conversion into carbonate is not complete. Mortar is known, under favourable circumstances, to acquire extreme hardness with age. Lime-cements which resist the action of water, contain the oxides of iron, silica, and alumina; they require to be carefully prepared, and the stone not over-heated. When ground to powder and mixed with water, solidification speedily ensues, from causes not yet thoroughly understood, and the cement, once in this condition, is unaffected by wet. Parker's or Roman cement is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay. Lime is of great importance in agriculture; it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is promoted, and other important objects, as the destruction of certain hurtful compounds of iron in marsh and peat-land, is often attained. The addition of lime probably serves likewise to liberate potassa from the insoluble silicate of that base contained in the soil.

Binoxide of Calcium, CaO_2. — This is stated to resemble binoxide of barium, and to be obtainable by a similar process.

Chloride of calcium, CaCl. — Usually prepared by dissolving marble in hydrochloric acid; also a by-product in several chemical manufactures. The salt separates from a strong solution in colourless, prismatic, and exceedingly deliquescent crystals, which contain 6 equivalents of water. By heat this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals reduced to powder are employed in the production of artificial cold by being mixed with snow or powdered ice; and the chloride, strongly dried or in a fused condition, is of great practical use in desiccating gases, for which purpose the latter are slowly transmitted through tubes

fragments of the salt. Chloride of calcium is also freely soluble , which, when anhydrous, forms with it a definite crystallizable

E OF CALCIUM. — The simple sulphide is obtained by reducing f lime at a high temperature by charcoal or hydrogen; it is nearly and but little soluble in water. — By boiling together hydrate of r, and flowers of sulphur, a red solution is obtained, which on posits crystals of bisulphide, which contain water. When the in excess, and the boiling long continued, a pentasulphide is ; hyposulphurous acid is, as usual, formed in these reactions.

IDE OF CALCIUM.—When the vapour of phosphorus is passed over of lime heated to redness in a porcelain tube, a chocolate-brown , the so-called *phosphide of lime*, is produced. This substance is mechanical mixture of phosphide of calcium, and phosphate of yields spontaneously inflammable phosphoretted hydrogen when ater.[1]

TE OF LIME; GYPSUM; SELENITE; CaO, SO_3.—Native sulphate of rystalline condition, containing 2 equivalents of water, is found in le abundance in some localities; it is often associated with rock- en regularly crystallized, it is termed *selenite*. Anhydrous sulphate also occasionally met with. The salt is formed by precipitation oderately concentrated solution of chloride of calcium is mixed uric acid. Sulphate of lime is soluble in about 500 parts of cold l its solubility is a little increased by heat. It is more soluble in taining chloride of ammonium or nitrate of potassa. The solution ated by alcohol. Gypsum, or native hydrated sulphate, is largely for the purpose of making casts of statues and medals, and also s in the porcelain and earthenware manufactures, and for other ns. It is exposed to heat in an oven where the temperature does l 260° (126°·6C), by which the water of crystallization is expelled, wards reduced to fine powder. When mixed with water, it solidifies ort time from the re-formation of the same hydrate; but this effect happen if the gypsum has been over-heated. It is often called Paris. Artificial coloured marbles, or *scagliola*, are frequently by inserting pieces of natural stone in a soft stucco containing this , and polishing the surface when the cement has become hard. of lime is one of the most common impurities of spring water. culiar property water acquires by the presence in it of lime, is *ardness*. It manifests itself by the effect such waters have upon e, and particularly by its peculiar behaviour with soap. Hard ald a lather with soap only after the whole of the lime-salts have wn down from the water in the form of an insoluble lime-soap. principle, Prof. Clark's soap-test for the hardness of waters is The hardness produced by sulphate of lime is called *permanent hard-* it cannot be remedied.

ATE OF LIME; CHALK; LIMESTONE; MARBLE; CaO, CO_2. — Carbo- me, often more or less contaminated by protoxide of iron, clay, and natter, forms rocky beds, of immense extent and thickness, in ery part of the world. These present the greatest diversities of nd appearance, arising, in a great measure, from changes to which

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ng to M. Paul Thenard, the phosphide of calcium existing in this mixture, has itions PCa_2. By coming in contact with water, it yields liquid phosphoretted $PCa_2 + 2HO = 2CaO + PH_2$ — (Page 166).
ter portion of the liquid phosphide is immediately decomposed into solid and sphoretted hydrogen. — $5PH_2 = 3PH_3 + P^2H$.
l of the Pharmaceutical Society, vol. vi. p. 526.

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they have been subjected since their deposition. The most ancient and highly crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviæ of once living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone and other rocks are very often lined with magnificent crystals of carbonate of lime or calcareous spar, which have evidently been slowly deposited from a watery solution. Carbonate of lime is always precipitated when an alkaline carbonate is mixed with a solution of that base.

Although this substance is not sensibly soluble in pure water, is is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of that gas, the turbidity first produced disappears on agitation, and a transparent solution of carbonate of lime in excess of carbonic acid is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that lime in this condition should be of very common occurrence; and such is really found to be the fact; river, and more especially spring water, almost invariably containing carbonate of lime thus dissolved. In limestone districts, this is often the case to a great extent. The *hardness* of water, which is owing to the presence of carbonate of lime, is called *temporary*, since it is diminished to a very considerable extent by boiling, and may be nearly removed by mixing the hard water with lime-water, when both the dissolved carbonate and the dissolved lime, which becomes thus carbonated, are precipitated. Upon this principle, Prof. Clark's process of softening water is based. This process is of considerable importance, since a supply of hard water to towns is in many respects a source of great inconvenience. As has been already mentioned, the use of such water, for the purposes of washing, is attended with a great loss of soap. Boilers in which such water is heated, speedily become lined with a thick stony incrustation.[1] The beautiful stalactitic incrustations of lime-stone caverns, and the deposits of calc-sinter or travertin upon various objects, and upon the ground in many places, are thus explained by the solubility of carbonate of lime in water containing carbonic acid.

Crystallized carbonate of lime exhibits the curious property of dimorphism; calcareous spar and arragonite, although possessing the same chemical composition, both containing single equivalents of lime and carbonic acid, and nothing besides, have different crystalline forms, different densities, and different optical properties.

The former occurs very abundantly in crystals derived from an obtuse rhomboid, whose angles measure 105° 5′ and 74° 55′: its density varies from 2·5 to 2·8. The rarer variety, or arragonite, is found in crystals whose primary form is a right rhombic prism; a figure having no geometrical relation to the preceding; it is, besides, heavier and harder.

PHOSPHATES OF LIME.—A number of distinct compounds of lime and phosphoric acid probably exist. Two *tribasic phosphates*, $2CaO,HO,PO_5$, and $3CaOPO_5$, are produced when the corresponding soda-salts are added in solution to chloride of calcium; the first is slightly crystalline, and the second gelatinous. When the first phosphate is digested with ammonia, or dissolved in acid and re-precipitated by that alkali, it is converted into the second.

[1] Many proposals have been made to prevent the formation of boiler-deposits. The most efficient appears to be the method of Dr. Ritterband, which consists in throwing into the boiler a small quantity of sal-ammoniac, when carbonate of ammonia is formed, which is volatilized with the steam, chloride of calcium remaining in solution. It need scarcely be mentioned that this plan is inapplicable in the case of permanently hard waters.

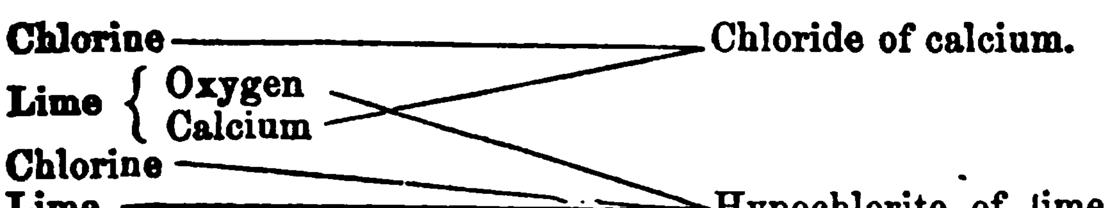
earth of bones consists principally of what appears to be a combi-
on of these two salts. Another phosphate, containing 2 equivalents asic water, has been described, which completes the series; it is formed lissolving either of the preceding in phosphoric, hydrochloric, or nitric , and evaporating until the salt separates on cooling in small platy crys- . It is this substance which yields phosphorus, when heated with char- , in the ordinary process of manufacture before described. *Bibasic* and *obasic phosphates of lime* also exist. These phosphates, although inso- e in water, dissolve readily in dilute acids, even acetic acid.

LUORIDE OF CALCIUM; FLUOR-SPAR; CaF.—This substance is important the most abundant natural source of hydrofluoric acid and the other rides. It occurs beautifully crystallized, in various colours, in lead-veins, crystals having commonly the cubic, but sometimes the octahedral form, llel to the faces of which latter figure they always cleave. Some varie- , when heated, emit a greenish phosphorescent light. The fluoride is insoluble in water, and is decomposed by oil of vitriol in the manner ady mentined, vide p. 149.

HLORIDE OF LIME; BLEACHING-POWDER.—When hydrate of lime, very htly moist, is exposed to chlorine gas, the latter is eagerly absorbed, and mpound produced which has attracted a great deal of attention; this is bleaching-powder of commerce, now manufactured on an immense scale, bleaching linen and cotton goods. It is requisite, in preparing this sub- ce, to avoid with the greatest care all elevation of temperature, which be easily done by slowly supplying the chlorine in the first instance. product, when freshly and well prepared, is a soft, white powder, which acts moisture from the air, and exhales an odour sensibly different from of chlorine. It is soluble in about 10 parts of water, the unaltered hy- e being left behind; the solution is highly alkaline, and bleaches feebly. n hydrate of lime is suspended in cold water, and chlorine gas trans- ed through the mixture, the lime is gradually dissolved, and the same liar bleaching compound produced; the alkalis also, either caustic or onated, may by similar means be made to absorb a large quantity of rine, and give rise to corresponding compounds; such are the "disinfect- solutions" of M. Labarraque.

he most consistent view of the constitution of these curious compounds at which supposes them to contain salts of hypochlorous acid, a substance emarkable for bleaching powers as chlorine itself; and this opinion seems e out by a careful comparison of the properties of the bleaching-salts those of the true hypochlorites. Hypochlorous acid can be actually ob- ed from good bleaching-powder, by distilling it with dilute sulphuric or ic acid, in quantity insufficient to decompose the whole; when the acid is l in excess, chlorine is disengaged.[1]

f this view be correct, chloride of calcium must be formed simultaneously the hypochlorite, as in the following diagram:—



n the temperature of the hydrate of lime has risen during the absorption he chlorine, or when the compound has been subsequently exposed to , its bleaching properties are impaired or altogether destroyed; it then ains chlorate of lime and chloride of calcium; oxygen, in variable quan-

[1] M. Gay-Lussac, Ann. Chim. et Phys. 3rd series, v. 296

fily, is usually set free. The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel it is speedily destroyed by the carbonic acid of the atmosphere. Commercial bleaching-powder thus constantly varies in value with its age, and with the care originally bestowed upon its preparation; the best may contain about 30 per cent. of available chlorine, easily liberated by an acid, which is, however, far short of the theoretical quantity.

The general method in which this substance is employed for bleaching is the following:—the goods are first immersed in a dilute solution of chloride of lime and then transferred to a vat containing dilute sulphuric acid. Decomposition ensues; both the lime of the hypochlorite and the calcium of the chloride are converted into sulphate of lime, while the free hypochlorous and hydrochloric acids yield water and free chlorine.

The chlorine thus disengaged in contact with the cloth, causes the destruction of the colouring matter. This process is often repeated, it being unsafe to use strong solutions. White patterns are on this principle imprinted upon coloured cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chloride bath, when the parts to which no acid has been applied remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, *as an aid to proper ventilation*, the bleaching-powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes it in the manner above described. An addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching-powder may be easily determined by the following method, in which the loosely combined chlorine is estimated by its effect in peroxidizing a protosalt of iron, of which two equivalents require one of chlorine; the latter acts by decomposing water and liberating a corresponding quantity of oxygen—78 (more correctly 78·16) grains of green sulphate of iron are dissolved in about two ounces of water, and acidulated by a few drops of sulphuric or hydrochloric acid; this quantity will require for peroxidation 10 grains of chlorine. Fifty grains of the chloride of lime to be examined are next rubbed up with a little tepid water, and the whole transferred to the alkalimeter[1] before described, which is then filled up to 0 with water, after which the contents are well mixed by agitation. The liquid is next gradually poured into the solution of iron, with constant stirring until the latter has become peroxidized, which may be known by a drop ceasing to give a deep blue precipitate with ferricyanide of potassium. The number of grain-measures of the chloride solution employed may then be read off, since these must contain 10 grains of serviceable chlorine, the quantity of the latter in the 50 grains may be easily reckoned. Thus, suppose 72 such measures have been taken, then

Measures.		Grs. chlorine.		Measures.		Grs. chlorine.
72	:	10	=	100	:	13·89

The bleaching-powder contains, therefore, 27·78 per cent.[2]

Baryta, strontia, and lime are thus distinguished from all other substances, and from each other.

Caustic potassa, when free from carbonate, and caustic ammonia, occasion no precipitates in dilute solutions of the earths, especially of the first two, the hydrates being soluble in water.

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[1] *Vide* p. 227.

[2] Graham's Elements, vol. i. p. [illegible]

Alkaline carbonates, and carbonate of ammonia, give white precipitates, soluble in excess of the precipitant, with all three.

Sulphuric acid, or a sulphate, added to very dilute solutions of the earths in question, gives an immediate white precipitate with baryta, a similar precipitate after a short interval with strontia, and occasions no change with the lime-salt. The precipitates with baryta and strontia are quite insoluble in nitric acid.

Solution of sulphate of lime gives an instantaneous cloud with baryta, and one with strontia after a little time. Sulphate of strontia is itself sufficiently soluble to occasion turbidity when mixed with chloride of barium.

Lastly, the soluble oxalates give a white precipitate in the most dilute solutions of lime, which is not dissolved by a drop or two of hydrochloric nor by an excess of acetic acid. This is an exceedingly characteristic test.

The chlorides of strontium and calcium dissolved in alcohol colour the flame of the latter red or purple; salts of baryta communicate to the flame a pale green tint.

MAGNESIUM.

A few pellets of sodium are placed at the bottom of a test-tube of hard German glass, and covered with fragments of fused chloride of magnesium. The heat of a spirit-lamp is then applied until reaction has been induced; this takes place with great violence and elevation of temperature, chloride of sodium being formed, and metallic magnesium set free. When the tube and its contents are completely cold, it is broken up, and the fragments put into cold water, by which the metal is separated from the salt.

Magnesium is a white, malleable metal, fusible at a red-heat, and not sensibly acted upon by cold water; it is oxidized by hot water. Heated in the air, it burns and produces magnesia, which is the only oxide. Sulphuric and hydrochloric acids dissolve it readily, evolving hydrogen.

The equivalent of this metal is 12, and its symbol Mg.

MAGNESIA; CALCINED MAGNESIA; MgO.—This is prepared with great ease by exposing the *magnesia alba* of pharmacy to a full red-heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a hydrate which possesses a feeble degree of solubility, requiring about 5,000 parts of water at 60° (15°·5C) and 36,000 parts at 212° (100°C). The alkalinity of magnesia can only be observed by placing a small portion in a moistened state upon test-paper; it neutralizes acids, however, in the most complete manner. It is infusible.

CHLORIDE OF MAGNESIUM, MgCl.—When magnesia, or its carbonate, is dissolved in hydrochloric acid, there can be no doubt respecting the simultaneous production of chloride of magnesium and water; but when this solution comes to be evaporated to dryness, the last portions of water are retained with such obstinacy, that decomposition of the water is brought about by the concurring attractions of magnesium for oxygen, and of chlorine for hydrogen; hydrochloric acid is expelled, and magnesia remains. If, however, sal-ammoniac or chloride of potassium happen to be present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to neutralize one with magnesia, and the other with ammonia, or carbonate of ammonia; to mix these solutions, evaporate them to dryness, and then expose the salt to a red-heat in a loosely covered porcelain crucible. Sal-ammoniac sublimes, and chloride of magnesium in a fused state remains; the latter is poured out upon a clean stone, and when cold, transferred to a well-stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent

and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in a melted state, it is converted into magnesia. It is soluble in alcohol.

SULPHATE OF MAGNESIA EPSOM SALT; MgO,SO_3+7HO.—This salt exists in sea-water, and in that of many mineral springs, and is now manufactured in large quantities by acting on magnesian lime-stone by diluted sulphuric acid, and separating the sulphate of magnesia from the greater part of the slightly soluble sulphate of lime by the filter. The crystals are derived from a right rhombic prism; they are soluble in an equal weight of water at 60° (15°·5C), and in a still smaller quantity at 212° (100°C). The salt has a nauseous bitter taste, and, like many other neutral salts, purgative properties. When exposed to heat, 6 equivalents of water readily pass off, the seventh being energetically retained. Sulphate of magnesia forms beautiful double salts with the sulphates of potassa and ammonia, which contain 6 equivalents of water of crystallization.

CARBONATE OF MAGNESIA.—The *neutral carbonate*, MgO,CO_2, occurs native in rhombohedral crystals, resembling those of calcareous spar, embedded in talc-slate: a soft earthy variety is sometimes met with.

When magnesia alba is dissolved in carbonic acid water, and the solution left to evaporate spontaneously, small prismatic crystals are deposited, which consist of carbonate of magnesia, with 3 equivalents of water.

The *magnesia alba* itself, although often called carbonate of magnesia, is not so in reality; it is a compound of carbonate with hydrate. It is prepared by mixing hot solutions of carbonate of potassa or soda, and sulphate of magnesia, the latter being kept in slight excess, boiling the whole a few minutes, during which time much carbonic acid is disengaged, and then well washing the precipitate so produced. If the solution be very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser. The composition of this precipitate is not perfectly constant. In most cases it contains $4(MgO,CO_2) + MgO,HO + 6HO$.

Magnesia alba is slightly soluble in water, especially when cold.

PHOSPHATE OF MAGNESIA, $2MgO,HO,PO_5 + 14HO$. — This salt separates in small colourless prismatic crystals when solutions of phosphate of soda and sulphate of magnesia are mixed and suffered to stand some time. Prof. Graham states that it is soluble in about 1,000 parts of cold water, but Berzelius describes a phosphate which only requires 15 parts of water for solution: this can hardly be the same substance. Phosphate of magnesia exists in the grain of the cereals, and can be detected in considerable quantity in beer.

PHOSPHATE OF MAGNESIA AND AMMONIA, $2MgO,NH_4O,PO_5+12HO$.—When a soluble phosphate is mixed with a salt of magnesia, and ammonia or its carbonate added, a crystalline precipitate, having the above composition, subsides immediately, if the solutions are concentrated, and after some time if very dilute; in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but scarcely so in saline liquids. When heated, it is resolved into bibasic phosphate (pyrophosphate) of magnesia, containing 35·71 per cent. of magnesia. At a strong red-heat it fuses to a white enamel-like mass. The phosphate of magnesia and ammonia sometimes forms an urinary calculus.

In practical analysis, magnesia is often separated from solutions by bringing it into this state. The liquid, free from alumina, lime, &c., is mixed with phosphate of soda and excess of ammonia, and gently heated for a short time. The precipitate is collected upon a filter and thoroughly washed with water containing a little sal-ammoniac, after which it is dried, ignited to redness and weighed. The proportion of magnesia is then easily calculated.

Silicates of magnesia.—The following natural compounds belong to this ass :—*Steatite* or *soap-stone*, MgO,SiO_3, a soft, white, or pale-coloured, amorous substance, found in Cornwall and elsewhere; *Meerschaum*, MgO,SiO_3 + O, from which pipe-bowls are often manufactured;—*Chrysolite*, $3MgO,SiO_3$, crystallized mineral, sometimes employed for ornamental purposes; a poron of magnesia is commonly replaced by protoxide of iron which communites a green colour;—*Serpentine* is a combination of silicate and hydrate of agnesia;—*Jade*, an exceedingly hard stone, brought from New Zealand, conins silicate of magnesia combined with silicate of alumina; its green lour is due to sesquioxide of chromium;—*Augite* and *hornblende* are sentially double salts of silicic acid, magnesia, and lime, in which the agnesia is more or less replaced by its isomorphous substitute, protoxide f iron.

The salts of magnesia are strictly isomorphous with those of the protoxles of zinc, of iron, of copper, &c.; they are usually colourless, and are asily recognised by the following characters:—

A gelatinous white precipitate with caustic alkalis, including ammonia, insoluble in excess, but soluble in solution of sal-ammoniac.

A white precipitate with the carbonates of potassa and soda, but *none* with carbonate of ammonia in the cold.

A white crystalline precipitate with soluble phosphates, on the addition of a little ammonia.

SECTION III.

METALS OF THE EARTHS PROPER.

ALUMINIUM OR ALUMINUM.

Alumina, the only known oxide of this metal, is a substance of very abundant occurrence in nature in the state of silicate, as in felspar and its associated minerals, and in the various modifications of clay thence derived. Aluminium is prepared in the same manner as magnesium, but with rather more difficulty; a platinum or iron tube closed at one extremity may be employed. Sesquichloride of aluminium is first introduced, and upon that about an equal bulk of potassium loosely wrapped in platinum foil. The lower part of the tube is then heated so as to sublime the chloride and bring its vapours in contact with the melted potassium. The reduction takes place with great disengagement of heat. The metal, separated by cold water from the alkaline chloride, has a tin-white colour and perfect lustre. It is obtained in small fused globules by the heat of reduction, which are malleable, and have a specific gravity of 2·6. When heated in the air or in oxygen, it takes fire and burns with brilliancy, producing alumina.

Aluminium has for its equivalent the number 13·7; its symbol is Al.

Alumina, Al_2O_3.—This substance is inferred to be a sesquioxide, from its isomorphism with the red oxide of iron. It is prepared by mixing solution of alum with excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of hydrate of alumina is thrown down. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, coherent mass, very little acted upon by acids. The hydrate, on the contrary, when simply dried in the air, or by gentle heat, dissolves freely in dilute acid, and in caustic potassa or soda, from which it is precipitated by the addition of sal-ammoniac. Alumina is fusible before the oxyhydrogen blowpipe. The mineral called *corundum*, of which the ruby and sapphire are transparent varieties, consists of nearly pure alumina in a crystallized state, with a little colouring oxide; emery, used for polishing glass and metals, is a coarse variety of corundum. Alumina is a very feeble base, and its salts have often an acid reaction.

Sesquichloride of aluminium, Al_2Cl_3.—The solution of alumina in hydrochloric acid behaves, when evaporated to dryness, like that of magnesia, the chloride being decomposed by the water, and alumina and hydrochloric acid produced. The chloride may be thus prepared:—Pure precipitated alumina is dried and mixed with lampblack, and the mixture strongly calcined in a covered crucible. It is then transferred to a porcelain tube fixed across a furnace, and heated to redness in a stream of chlorine gas, when the alumina, yielding to the attraction of the chlorine on the one hand, and the carbon on the other, for each of its constituents, suffers decomposition, carbonic oxide being disengaged, and sesquichloride of aluminium formed; the latter sublimes, and condenses in the cool part of the tube.

Sesquichloride of aluminium is a crystalline yellowish substance, excessively greedy of moisture, and very soluble. Once dissolved, it cannot be again recovered. It is said to combine with sulphuretted and phosphoretted hydrogen, and with ammonia.

Sulphate of alumina, $Al_2O_3,3SO_3+18HO$. — Prepared by saturating dilute sulphuric acid with hydrate of alumina, and evaporating. It crystallizes in thin, pearly plates, soluble in 2 parts of water; it has a sweet and astringent taste, and an acid reaction. Heated to redness, it is decomposed, leaving pure alumina. Two other sulphates of alumina, with excess of base, are also described, one of which is insoluble in water.

Sulphate of alumina combines with the sulphates of potassa, soda, and ammonia, forming double salts of great interest, the *alums*. Common alum, the source of all the preparations of alumina, contains $Al_2O_3,3SO_3+KO,SO_3+24HO$. It is manufactured, on a very large scale, from a kind of slaty clay, loaded with bisulphide of iron, which abounds in certain parts. This is gently roasted, and then exposed to the air in a moistened state; oxygen is absorbed, the sulphur becomes acidified, sulphate of protoxide of iron and sulphate of alumina are produced, and afterwards separated by lixiviation with water. The solution is next concentrated, and mixed with a quantity of chloride of potassium, which decomposes the iron-salt, forming protochloride of iron and sulphate of potassa, which latter combines, with the sulphate of alumina, to alum. By crystallization, the alum is separated from the highly soluble chloride of iron, and afterwards easily purified by a repetition of that process. Other methods of alum-making exist, and are sometimes employed. Potassa-alum crystallizes in colourless, transparent octahedrons, which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus paper, and dissolves in 18 parts of water at 60° (15°·5C), and in its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and, by a very high temperature, decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, &c.; it is occasionally contaminated with oxide of iron, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathic rock, altered by sulphurous vapours, was once much prized on account of its freedom from this impurity.

A mixture of dried alum and sugar, carbonized in an open pan, and then heated to redness, out of contact of air, furnishes the *pyrophorus of Homberg*, which ignites spontaneously on exposure to the atmosphere. The essential ingredient is, in all probability, finely divided sulphide of potassium.

Soda-alum, in which sulphate of soda replaces sulphate of potassa, has a form and constitution similar to that of the salt described; it is, however, much more soluble, and difficult to crystallize.

Ammonia-alum, containing NH_4O,SO_3, instead of KO,SO_3, very closely resembles common potassa-alum, having the same figure, and appearance, and constitution, and nearly the same degree of solubility as that substance It is sometimes manufactured for commercial use. When heated to redness, it yields pure alumina.

Few of the other salts of alumina, except the silicates, present points of interest; these latter are of great importance. Silicates of alumina enter into the composition of a number of crystallized minerals, among which felspar occupies, by reason of its abundant occurrence, a prominent place. Granite, porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under peculiar circumstances, by no means well understood, and particularly by the action of the carbonic acid of the air, suffers complete decomposition, becoming converted into a soft, friable mass of earthy matter. This is the origin of clay; the change itself is seen

in great perfection in certain districts of Devonshire and Cornwall, the felspar of the fine white granite of those localities being often disintegrated to an extraordinary depth, and the rock altered to a substance resembling soft mortar. By washing, this finely divided matter is separated from the quartz and mica, and the milk-like liquid, being collected in tanks and suffered to stand, deposits the suspended clay, which is afterwards dried, first in the air and afterwards in a stove, and employed in the manufacture of porcelain. The composition assigned to unaltered felspar is Al_2O_3, $3SiO_3 + KO,SiO_3$, or alum, having silicic acid in the place of sulphuric. The exact nature of the change by which it passes into porcelain clay is unknown, although it evidently consists in the abstraction of silica and alkali.[1]

When the decomposing rock contains oxide of iron, the clay produced is coloured. The different varieties of shale and slate result from the alteration of ancient clay-beds, apparently in many instances by the infiltration of water holding silica in solution; the dark appearance of some of these deposits is due to bituminous matter.

It is a common mistake to confound clay with alumina; all clays are essentially silicates of that base; they often vary a good deal in composition. Dilute acids exert little action on these compounds; but by boiling with oil of vitriol, alumina is dissolved out, and finely divided silica left behind. Clays containing an admixture of carbonate of lime are termed marls, and are recognized by effervescing with acids.

A basic silicate of alumina, $2Al_2O_3$, SiO_3, is found crystallized, constituting the beautiful mineral called *cyanite*. The compounds formed by the union of the silicates of alumina with other silicates are almost innumerable; a soda-felspar, *albite*, containing that alkali in place of potassa, is known, and there are two somewhat similar lithia-compounds *spodumene* and *petalite*. The *zeolites* belong to this class: *analcime*, *nepheline*, *mesotype*, &c., are double silicates of soda and alumina, with water of crystallization. *Stilbite*, *heulandite*, *laumonite*, *prehnite*, &c., consist of silicate of lime, combined with silicate of alumina. The *garnets*, *axinite*, *mica*, &c., have a similar composition, but are anhydrous. Sesquioxide of iron is very often substituted for alumina in these minerals.

Alumina, when in solution, is distinguished without difficulty.

Caustic potassa and soda occasion white gelatinous precipitates of hydrate of alumina, freely soluble in excess of the alkali.

Ammonia produces a similar precipitate, insoluble in excess of the reagent.

The alkaline carbonates and carbonate of ammonia precipitate the hydrate, with escape of carbonic acid. The precipitates are insoluble in excess.

BERYLLIUM (GLUCINUM).

This metal is prepared from the chloride in the same manner as aluminium. It is fusible with great difficulty, not acted upon by cold water and burns when heated in the air, producing berylla.

The equivalent of beryllium is 6·9, and the symbol Be.

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[1] A specimen of white porcelain clay from Dartmoor, Devon, gave the author the following result on analysis:—

Silica	47·20
Alumina, with trace of iron and manganese	38·80
Lime	0·24
Water	12·00
Alkali and loss	1·76
	100·00

A, Be_2O_3, is a rare earth found in the *emerald*, *beryl*, and *euclase*,
h it may be extracted by a tolerably simple process. It very much
alumina, but is distinguished from that substance by its solubility,
hly precipitated, in a cold solution of carbonate of ammonia, from
s again thrown down on boiling. The salts of berylla have a sweet
ence its former name glucina (γλυκύς).

YTTRIUM.

tal of a very rare earth, *yttria*, contained in a few scarce minerals.
is derived from Ytterby, a place in Sweden, where one of these,
is found. It is obtained from the chloride by the process already
; it resembles in character the preceding metal.
y yttria is stated by Professor Mosander to be a mixture of the
not less than three metals, namely, *Yttrium*, *erbium*, and *terbium*,
fer in the characters of their salts, and in other particulars. The
very powerful base, the two others are weak ones. They are
with extreme difficulty.

CERIUM, LANTHANIUM, AND DIDYMIUM.

ides of these very rare metals are found associated in the Swedish
erite; the equivalent of cerium is about 47, and its symbol Ce.
l forms a protoxide CeO, and a sesquioxide Ce_2O_3.
ude sesquioxide of cerium obtained by precipitating the double
of cerium and potassa directly derived from cerite by carbonate of
as been shown by Mosander to contain in addition to sesquioxide
, the oxides of two other metals, to which the above names were
fter ignition it is red-brown. The complete separation of these
lies is attended with the greatest difficulty, and has indeed been
ially accomplished.[1] Oxide of cerium may be obtained pure by
he mixture of the three oxides first with diluted and afterwards
entrated nitric acid, which gradually removes the whole of the
lathanium and didymium.
llow oxide of cerium, obtained by igniting the nitrate, is a mixture
and sesquioxide, which are extremely difficult to obtain in a sepa-
. The salts of the former are colourless, and are completely pre-
by sulphate of potassa; the sulphate of the sesquioxide is yellow,
s a beautiful double salt with sulphate of potassa, which is decom-
water. The metal cerium has been obtained from the chloride by
of sodium.
f lanthanium, as pure as it has been obtained, forms a very pale
loured powder, unchanged by ignition in open or close vessels. In
ith water it gives a snow-white bulky hydrate which has an alkaline
and decomposes ammoniacal salts by boiling. Its salts are
able, colourless, sweet, and astringent, and are precipitated by
of potassa.
ably pure lanthanium-salt may be obtained by slowly crystallizing
olution containing the sulphates of lanthanium and didymium,
ut the rose-coloured crystals (containing didymium), and the violet
taining lanthanium and didymium), adding the solution of the latter
ther-liquor, and repeating the process. In this manner the whole
dymium-salt may be finally separated by crystallization. Metallic
m is prepared like cerium.
asional brown colour of crude oxide of cerium is due to oxide of

[1] sis of the various methods for the separation of cerium, lanthanium, and didy
een given by Mr. H. Watts. Chem. Soc. Quar. Jour. ii. 140.

didymium. In a pure state, it forms a brown powder, soluble in acids, and generating a series of red crystallizable salts, from which caustic potash precipitates a violet-blue hydrate, quickly changing by exposure to the air. It communicates to glass an amethystine colour.[1]

ZIRCONIUM.

Prepared by heating the double fluoride of zirconium and potassium with potassium, and separating the salt with cold water. The metal is black, and acquires a feeble lustre when burnished. It takes fire when heated in the air.

The equivalent of zirconium is 33·6, and its symbol Zr.

Zirconia, Zr_2O_3, is a rare earth, very closely resembling alumina, found together with silica, in the mineral *zircon*. The salts are colourless and have an astringent taste.

Svanberg has rendered it probable that an undescribed metallic oxide exists in certain varieties of zircon, for the metal of which he proposes the name of *norium*.

THORIUM.

The metal of an earth from a very rare mineral, *thorite*; it agrees in character with aluminium, and is obtained by similar means.

The equivalent of thorium is 59·6, and its symbol Th.

Thoria, ThO, is remarkable for its great specific gravity, and is otherwise distinguished by peculiar properties which separate it from all other substances.

Manufacture of Glass, Porcelain, and Earthenware.

Glass.—Glass is a mixture of various insoluble silicates, with excess of silica, altogether destitute of crystalline structure: the simple silicates, formed by fusing the bases with silicic acid in equivalent proportions, very often crystallize, which happens also with the greater number of the natural silicates included among the earthly minerals. Compounds identical with some of these are also occasionally formed in artificial processes, where large masses of melted glassy matter are suffered to cool slowly. The alkaline silicates, when in a state of fusion, have the power of dissolving a large quantity of silica.

Two principal varieties of glass are met with in commerce, namely, glass composed of silica, alkali, and lime, and glass containing a large proportion of silicate of lead; *crown* and *plate-glass* belong to the former division; *flint-glass*, and the material of artificial gems to the latter. The lead promotes fusibility, and confers also density and lustre. Common green bottle glass contains no lead, but much silicate of black oxide of iron, derived from the impure materials. The principle of the glass manufacture is very simple. Silica, in the shape of sand, is heated with carbonate of potassa or soda, and slaked lime or oxide of lead; at a high temperature, fusion and combination occur, and the carbonic acid is expelled. When the melted mass has become perfectly clear and free from air-bubbles, it is left to cool until it assumes the peculiar tenacious condition proper for working.

The operation of fusion is conducted in large crucibles of refractory fire-clay, which in the case of lead-glass are covered by a dome at the top, and have an opening at the side by which the materials are introduced and the melted glass withdrawn. Great care is exercised in the choice of the sand, which must be quite white and free from oxide of iron. Red-lead, one of the higher oxides, is preferred to litharge, although immediately reduced to

[1] Annalen der Chemie und Pharmacie, xlviii. 210.

rotoxide by the heat, the liberated oxygen serving to destroy any combustible matter which might accidentally find its way into the crucible and stain ie glass by reducing a portion of the lead. Potassa gives a better glass ian soda, although the latter is very generally employed, from its lower rice. A certain proportion of broken and waste glass of the same kind is ways added to the other materials.

Articles of blown glass are thus made:—The workman begins by collectg a proper quantity of soft, pasty glass at the end of his *blow-pipe*, an on tube, five or six feet in length, terminated by a mouth-piece of wood; then commences blowing, by which the lump is expanded into a kind of isk, susceptible of having its form modified by the position in which it is ld, and the velocity of rotation continually given to the iron tube. If an en-mouthed vessel is to be made, an iron rod, called a *pontil* or *puntil*, is pped into the glass-pot and applied to the bottom of the flask, to which it us serves as a handle, the blowpipe being removed by the application of a ld iron to the neck. The vessel is then re-heated at a hole left for the irpose in the wall of the furnace, and the aperture enlarged, and the vessel herwise altered in figure by the aid of a few simple tools, until completed. is then detached, and carried to the annealing oven, where it undergoes ow and gradual cooling during many hours, the object of which is to obvie the excessive brittleness always exhibited by glass which has been iickly cooled. The large circular *tables* of crown-glass are made by a very irious process of this kind; the globular flask at first produced, transrred from the blowpipe to the pontil, is suddenly made to assume the form a flat disc by the centrifugal force of the rapid rotatory movement given the rod. Plate-glass is cast upon a flat metal table, and after very carel annealing, ground true and polished by suitable machinery. Tubes are ade by rapidly drawing out a hollow cylinder; and from these a great vaety of useful apparatus may be constructed with the help of a lamp and owpipe, or still better, the bellows-table of the barometer-maker. Small bes may be bent in the flame of a spirit-lamp or gas-jet, and cut with eat ease by a file, a scratch being made, and the two portions pulled or oken asunder in a way easily learned by a few trials.

Specimens of the two chief varieties of glass gave the following results analysis:—

Bohemian plate-glass (excellent).[1]

Silica	60·0
Potassa	25·0
Lime	12·5
	97·5

English flint-glass.[2]

Silica	51·93
Potassa	13·77
Oxide of lead	33·28
	98·98

The difficultly-fusible white Bohemian tube, so invaluable in organic chestry, has been found to contain in 100 parts:—

Silica	72·80
Lime, with trace of alumina	9·68
Magnesia	·40
Potassa	16·80
Traces of manganese, &c., and loss	·32

Different colours are often communicated to glass by metallic oxides. us, oxide of cobalt gives deep blue; oxide of manganese, amethyst; subide of copper, ruby-red; black oxide of copper, green; the oxides of n, dull green or brown, &c. These are either added to the melted con

[1] *Mitscherlich, Lehrbuch, ii. 187.*

[2] Faraday.

tents of the glass-pot, in which they dissolve, or applied in a particular manner to the surface of the plate or other object, which is then re-heated until fusion of the colouring matter occurs; such is the practice of enamelling and glass-painting. An opaque white appearance is given by oxide of tin; the enamel of watch-faces is thus prepared.

When silica is melted with twice its weight of carbonate of potassa or soda, and the product treated with water, the greater part dissolves, yielding a solution from which acids precipitate gelatinous silica. This is the *soluble glass* sometimes mentioned by chemical writers; its solution has been used for rendering muslin and other fabrics of cotton or linen less combustible.

PORCELAIN AND EARTHENWARE. — The plasticity of natural clays, and their hardening when exposed to heat, are properties which suggested in very early times their application to the making of vessels for the various purposes of daily life; there are few branches of industry of higher antiquity than that exercised by the potter.

True porcelain is distinguished from earthenware by very obvious characters. In porcelain the *body* of the ware is very compact and translucent, and breaks with a conchoidal fracture, symptomatic of a commencement of fusion. The glaze, too, applied for giving a perfectly smooth surface, is closely adherent, and in fact graduates by insensible degrees into the substance of the body. In earthenware, on the contrary, the fracture is open and earthy, and the glaze detachable with greater or less facility. The compact and partly glassy character of porcelain is the result of the admixture with the clay of a small portion of some substance, fusible at the temperature to which the ware is exposed when baked or fired, and which, absorbed by the more infusible portion, binds the whole into a solid mass on cooling; such substances are found in felspar, and in a small admixture of silicate of lime, or alkali. The clay employed in porcelain-making is always directly derived from the decomposed felspar, none of the clays of the secondary strata being pure enough for the purpose; it must be white, and free from oxide of iron. To diminish the retraction which this substance undergoes in the fire, a qantity of finely divided silica, carefully prepared by crushing and grinding calcined flints or chert, is added, together with a proper proportion of felspar or other fusible material, also reduced to impalpable powder. The utmost pains are taken to effect perfect uniformity of mixture, and to avoid the introduction of particles of grit or other foreign bodies. The ware itself is fashioned either on the potter's wheel;—a kind of vertical lathe;—or in moulds of plaster of Paris, and dried, first in the air, afterwards by artificial heat, and at length completely hardened by exposure to the temperature of ignition. The porous *biscuit* is now fit to receive its glaze, which may be either ground felspar, or a mixture of gypsum, silica, and a little porcelain clay, diffused through water. The piece is dipped for a moment into this mixture, and withdrawn; the water sinks into its substance, and the powder remains evenly spread upon its surface; it is once more dried, and lastly, fired at an exceedingly high temperature.

The porcelain-furnace is a circular structure of masonry, having several fire-places, and surmounted by a lofty dome. Dry wood or coal is consumed as fuel, and its flame directed into the interior, and made to circulate around and among the earthen cases, or *seggars* in which the articles to be fired are packed. Many hours are required for this operation, which must be very carefully managed. After the lapse of several days, when the furnace has completely cooled, the contents are removed in a finished state, so far as regards the ware.

The ornamental part, consisting of gilding and painting in enamel, has yet to be executed, after which the pieces are again heated, in order to flux the colours. This operation has sometimes to be repeated more than once.

celain in Europe is of modern origin; the Chinese
the commencement of the seventh century, and
cts, altogether unequalled. The materials em·
to be *kaolin*, or decomposed felspar: *petuntze*, or
der; and the ashes of fern, which contain carbonate

is a coarse kind of porcelain, made from clay containing
ttle lime, to which it owes its partial fusibility. The gla-
, throwing common salt into the heated furnace; this is vo-
mposed by the joint agency of the silica of the ware, and
water always present; hydrochloric acid and soda are pro-
er forming a silicate, which fuses over the surface of the ware,
ain, but excellent glaze.

WARE. — The finest kind of earthenware is made from a white
clay, mixed with a considerable quantity of silica. The articles
oughly dried and fired, after which they are dipped into a readily
glaze-mixture, of which oxide of lead is usually an important ingre-
, and, when dry, re-heated to the point of fusion of the latter. The
le process is much easier of execution than the making of porcelain, and
ands less care. The ornamental designs in blue and other colours, so
mon upon plates and household articles, are printed upon paper in enamel
ent, mixed with oil, and transferred, while still wet, to the unglazed
e. When the ink becomes dry, the paper is washed off, and the glazing
pleted.

he coarser kinds of earthenware are sometimes covered with a whitish
que glaze, which contains the oxides of lead and tin; such glaze is very
le to be attacked by acids, and is dangerous for culinary vessels.

rucibles when of good quality, are very valuable to the practical chemist.
y are made of clay free from lime, mixed with sand or ground ware of
same description. The Hessian and Cornish crucibles are among the
t. Sometimes a mixture of plumbago and clay is employed for the same
pose; and powdered coke has been also used with the earth; such cru-
les bear rapid changes of temperature with impunity.

SECTION IV.

OXIDABLE METALS PROPER, WHOSE OXIDES FORM POWERFUL BASES.

MANGANESE.

Manganese is tolerably abundant in nature in an oxidized state, forming or entering into the composition of, several interesting minerals. Traces of this substance are very frequently found in the ashes of plants.

Metallic manganese, or perhaps, strictly, carbide of manganese, may be best prepared by the following process. The carbonate is calcined in an open vessel, by which it becomes converted into a dense brown powder; this is intimately mixed with a little charcoal, and about one-tenth of its weight of anhydrous borax. A charcoal crucible is next prepared by filling a Hessian or Cornish crucible with moist charcoal-powder, introduced a little at a time, and rammed as hard as possible. A smooth cavity is then scooped in the centre, into which the above-mentioned mixture is compressed, and covered with charcoal-powder. The lid of the crucible is then fixed, and the whole arranged in a very powerful wind-furnace. The heat is slowly raised until the crucible becomes red-hot, after which it is urged to its maximum for an hour or more. When cold, the crucible is broken up, and the metallic button of manganese extracted.

Manganese is a greyish-white metal, resembling some varieties of cast-iron; it is hard and brittle, and destitute of magnetic properties. Its specific gravity is about 8. It is fusible with great difficulty, and, when free from iron, oxidizes in the air so readily, that it requires to be preserved in naphtha. Water is not sensibly decomposed by manganese in the cold. Dilute sulphuric acid dissolves it with great energy, evolving hydrogen.

The equivalent of manganese is assumed to be 27·6; its symbol is Mn.

Oxides of Manganese.—Seven different oxides of this metal are described, but two out of the number are, probably, secondary compounds.

Protoxide	MnO
Sesquioxide	Mn_2O_3
Binoxide	MnO_2
Proto-sesquioxide (red oxide)	$Mn_3O_4 = MnO, Mn_2O_3$
Varvicite	$Mn_4O_7 = Mn_2O_3 2MnO_2$
Manganic acid	MnO_3
Permanganic acid	Mn_2O_7

Protoxide, MnO. — When carbonate of manganese is heated in a stream of hydrogen gas, or of vapour of water, the carbonic acid is disengaged, and a green-coloured powder left behind, which is the protoxide. Prepared at a dull red-heat only, the protoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change; but when at a higher temperature it appears more stable. This oxide is a very powerful

se, being isomorphous with magnesia and zinc; it dissolves quietly in ute acids, neutralizing them completely and forming salts, which have ten a beautiful pink colour. When alkalis are added to solutions of these mpounds the white hydrated oxide first precipitated speedily becomes own by passing into a higher state of oxidation.

SESQUIOXIDE, Mn_2O_3. — This compound occurs in nature in the state of 'drate; a very beautiful crystallized variety is found at Ilefeld, in the artz. It is produced artificially, by exposing to the air the hydrated prot-ide, and forms the principal part of the residue left in the iron retort when ygen gas is prepared by exposing the native binoxide to a moderate red-at. The colour of the sesquioxide is brown or black, according to its igin or mode of preparation. It is a feeble base, isomorphous with alu-ina; for, when gently heated with diluted sulphuric acid, it dissolves to a d liquid, which, on the addition of sulphate of potassa or of ammonia, posits octahedral crystals having the constitution of common alum; these e, however, decomposed by water. Strong nitric acid resolves this oxide ito a mixture of protoxide and binoxide, the former dissolving, and the tter remaining unaltered; while hot oil of vitriol destroys it by forming lphate of the protoxide, and liberating oxygen gas. Heated with hydro-loric acid, chlorine is evolved, as with the binoxide, but to a smaller extent.

BINOXIDE, MnO_2.—The most common ore of manganese; it is found both assive and crystallized. It may be obtained artificially in the anhydrous tate by gently calcining the nitrate, or in combination with water, by adding olution of bleaching-powder to a salt of the protoxide. Binoxide of man-anese has a black colour, is insoluble in water, and refuses to unite with cids. It is decomposed by hot hydrochloric acid and by oil of vitriol in the ame manner as the sesquioxide.

As this substance is an article of commerce of considerable importance, eing used in a very large quantity for making chlorine, and as it is subject o great alteration of value from an admixture of the sesquioxide and several mpurities, it becomes desirable to possess means of assaying different sam-les that may be presented, with a view of testing their fitness for the pur-oses of the manufacturer. One of the best and most convenient methods s the following: — 50 grains of the mineral, reduced to a very fine powder, re put into the little vessel employed in the analysis of carbonates,[1] together ith about half an ounce of cold water, and 100 grains of strong hydro-hloric acid; 50 grains of crystallixed oxalic acid are then added, the cork arrying the chloride of calcium tube is fitted, and the whole quickly eighed or counterpoised. The application of a gentle heat suffices to deter-nine the action: the disengaged chlorine converts the oxalic acid into car-onic acid, with the help of the elements of water, two equivalents of car-onic acid representing one of chlorine, and consequently one of binoxide f manganese. Now, the equivalent of the latter substance, 43·6, is so early equal to twice that of carbonic acid, 22, that the loss of weight uffered by the apparatus when the reaction has has become complete, and he residual gas has been driven off by momentary ebullition, may be taken o represent the quantity of real binoxide in the 50 grains of the sample. t is obvious that the little apparatus of Will and Fresenius, described at age 229, may be used with the same advantage.

RED OXIDE, Mn_3O_4, or probably $MnO + Mn_2O_3$. — This oxide is also found ative, and is produced artificially by heating to whiteness the binoxide or squioxide, or by exposing the protoxide or carbonate to a red-heat in an pen vessel. It is a reddish-brown substance, incapable of forming salts, d acted upon by acids in the same manner as the two higher oxides already

[1] See page 228.

described. Borax and glass in a fused state dissolve this substance, and acquire the colour of the amethyst.

Varvicite, Mn_4O_7, or $Mn_2O_3+2MnO_2$. — A natural production, discovered by Mr. Phillips, among certain specimens of manganese-ore from Warwickshire; it has also been found at Ilefeld. It much resembles the binoxide, but is harder and more brilliant, and contains water. By a strong heat, varvicite is converted into red oxide, with disengagement of aqueous vapour and oxygen gas.

Chloride of manganese, MnCl. — This salt may be prepared in a state of purity from the dark brown liquid residue of the preparation of chlorine from binoxide of manganese and hydrochloric acid, which often accumulates in the laboratory to a considerable extent in the course of investigation, from the pure chloride, the carbonate and all other salts can be conveniently obtained. The liquid referred to consists chiefly of the mixed chlorides of manganese and iron; it is filtered, evaporated to perfect dryness, and then slowly heated to dull ignition in an earthen vessel, with constant stirring. The chloride of iron is thus either volatilized or converted by the remaining water into insoluble sesquioxide, while the manganese-salt is unaffected. On treating the greyish-looking powder thus obtained with water, the chloride of manganese is dissolved out, and may be separated by filtration from the sesquioxide of iron. Should a trace of the latter yet remain, it may be got rid of by boiling the liquid for a few minutes with a little carbonate of manganese. The solution of chloride has usually a delicate pink colour, which becomes very manifest when the salt is evaporated to dryness. A strong solution deposits rose-coloured tabular crystals, which contain 4 equivalents of water; these are very soluble and deliquescent. The chloride is fusible at a red-heat, is decomposed slightly at that temperature by contact of air, and is dissolved by alcohol, with which it forms a crystallizable compound.

Sesquichloride, Mn_2Cl_3. — When precipitated sesquioxide of manganese is put into cold dilute hydrochloric acid, it dissolves quietly, forming a red solution of sesquichloride. Heat disengages chlorine, and occasions the production of protochloride.

Sulphate of protoxide of manganese, MnO,SO_3+7HO. — A beautiful rose-coloured and very soluble salt, isomorphous with sulphate of magnesia. It is prepared on a large scale for the use of the dyer, by heating, in a close vessel, binoxide of manganese and coal, and dissolving the impure protoxide thus obtained in sulphuric acid, with the addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red-heat, by which the sulphate of sesquioxide of iron is decomposed. Water then dissolves out the pure sulphate of manganese, leaving the sesquioxide of iron behind. The salt is used to produce a permanent brown dye, the cloth steeped in the solution being afterwards passed through a solution of bleaching-powder, by which the protoxide is changed to insoluble hydrate of the binoxide. Sulphate of manganese sometimes crystallizes with five equivalents of water. It forms a double salt with sulphate of potassa.

Carbonate of manganese. — Prepared by precipitating the protochloride by an alkaline carbonate. It is insoluble and buff-coloured, or sometimes nearly white. Exposed to heat, it loses carbonic acid, and absorbs oxygen.

Manganic acid, MnO_3. — When an oxide of manganese is fused with an alkali, an additional quantity of oxygen is taken up from the air, and a deep green saline mass results, which contains a salt of the new acid, thus formed under the influence of the base. The addition of nitre, or chlorate of potassa, facilitates the production of manganic acid. Water dissolves this compound very readily, and the solution, concentrated by evaporation in vacuo, yields green crystals.

ıNGANIC ACID, Mn_2O_7. — When manganate of potassa, free from any cess of alkali, is put into a large quantity of water, it is resolved ırated binoxide of manganese, which subsides, and a deep purple ontaining permanganate of potassa. This effect is accelerated by 'he changes of colour accompanying this decomposition are very re- e, and have procured for the substance the name *mineral chameleon;* f alkali hinders, in some measure, the reaction, by conferring greater on the manganate. Permanganate of potassa is easily prepared on erable scale. Equal parts of very finely powdered binoxide of man- ınd chlorate of potassa are mixed with rather more than one part of of potassa dissolved in a little water, and the whole exposed, after tion to dryness, to a temperature just short of ignition. The mass d with hot water, the insoluble oxide separated by decantation, and ı purple liquid concentrated by heat, until crystals form upon its ; it is then left to cool. The crystals have a dark purple colour, and very soluble in cold water. The manganates and permanganates are ısed by contact with organic matter; the former are said to be iso- ıs with the sulphates, and the latter with the perchlorates.

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of the protoxide of manganese are very easily distinguished by ı.

ıxed caustic alkalis, and ammonia, give white precipitates, insoluble s, quickly becoming brown.

arbonates of the fixed alkalis, and carbonate of ammonia, give white ıtes, but little subject to change, and insoluble in excess of carbonate ınia.

uretted hydrogen gives no precipitate, but sulphide of ammonium lown insoluble, flesh-coloured sulphide of manganese, which is very ıristic.

cyanide of potassium gives a white precipitate.

anese is also easily detected by the blowpipe; it gives with borax an tine bead in the outer or oxidizing flame, and a colourless one in the me. Heated upon platinum foil with carbonate of soda, it yields a ass of manganate of soda.

IRON.

ıs by very far the most important member of the group of metals ıscussion; there are few substances to which it yields in interest, is considered how very intimately the knowledge of the properties ı of iron is connected with human civilization.

lic iron is of exceedingly rare occurrence; it has been found at in Connecticut,[1] forming a vein about two inches thick in mica-slate, ıvariably enters into the composition of those extraordinary stones o fall from the air, called *meteorites.* Isolated masses of soft malleable ı, of large dimensions, lie loose upon the surface of the earth in South . and elsewhere, and are presumed to have had a similar origin: tter contain, in common with the iron of the undoubted meteorites, In an oxidized condition, the presence of iron may be said to be l; it constitutes great part of the common colouring matter of rocks ı; it is contained in plants, and forms an essential component of the the animal body. In the state of bisulphide it is also very common. ın may be prepared, according to Mitscherlich, by introducing into

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[1] *Phillip's* Mineralogy, fourth edit. p. 208.

a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black oxide of iron. This is covered with a mixture of white sand, lime, and carbonate of potassa, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high degree of heat. A button of pure metal is thus obtained, the traces of carbon and silicum present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white colour and perfect lustre; it is extremely soft and tough, and has a specific gravity of 7.8. The crystalline form is probably the cube, to judge from appearances now and then exhibited. In good bar-iron or wire a distinct fibrous texture may always be observed when the metal has been attacked by rusting or by the application of an acid, and upon the perfection of this fibre much of its strength and value depends. Iron is the most tenacious of all the metals, a wire $\frac{1}{10}$th of an inch in diameter bearing a weight of 60lb. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron pressed or hammered together in this state cohere into a single mass; the operation is termed *welding*, and is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied; clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidize in dry air at common temperatures; heated to redness, it becomes covered with a scaly coating of black oxide, and at a high white-heat burns brilliantly, producing the same substance; in oxygen gas the combustion occurs with still greater ease. The finely divided spongy metal, prepared by reducing the oxide by hydrogen gas, takes fire spontaneously in the air.[1] Pure water, free from air and carbonic acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the sesquioxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapour.[2] At a red-heat iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely with separation of hydrogen. Iron is strongly magnetic up to a red-heat, when it loses all traces of that remarkable property.

The equivalent of iron is 28, and its symbol Fe.

Four compounds of iron and oxygen are described.

Protoxide	FeO
Sesquioxide (peroxide)	Fe_2O_3
Protosesquioxide (black oxide)	$Fe_3O_4 = FeO, Fe_2O_3$
Ferric acid	FeO_3

Protoxide, FeO. — This is a very powerful base, neutralising acids completely, and isomorphous with magnesia, oxide of zinc, &c. It is almost unknown in a separate state, from its extreme proneness to absorb oxygen and pass into the sesquioxide. When a salt of this substance is mixed with caustic alkali or ammonia, a bulky whitish precipitate of hydrate of the protoxide falls, which becomes nearly black when boiled, the water being separ-

[1] When obtained at a heat below redness.—R. B.

[2] The rusting of iron proceeds with rapidity after it once begins, extending from the part first affected. Iron rust contains ammonia, resulting from the combination of the nascent hydrogen of decomposed water uniting with dissolved nitrogen. This is an important point in medico-legal investigations, as it is considered, that, when stains on a steel instrument yield ammonia by the action of potassa, the presence of organic matter is proved; but as rust *contains* ammonia, it becomes necessary to ascertain its absence, or drive it off, previous to *operating* with potassa.—R. B.

ted. This hydrate exposed to the air, very rapidly changes, becoming green and ultimately red-brown. The soluble salts of protoxide of iron have commonly a delicate pale green colour, and a nauseous *metallic* taste.

SESQUIOXIDE, Fe_2O_3. — A feeble base, isomorphous with alumina. Sesquioxide of iron occurs native, most beautifully crystallized as specular iron ore the island of Elba, and elsewhere; also as red and brown *hæmatites*, the latter being a hydrate. It is artificially prepared by precipitating a solution sulphate of the sesquioxide or the sesquichloride of iron by excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced; fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red colour, and is used as a pigment, being prepared for the purpose by calcination of the sulphate of the protoxide; the tint varies somewhat with the temperature to which it has been exposed. This oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Sesquioxide of iron is not acted upon by the magnet.[1]

BLACK OXIDE; MAGNETIC OXIDE; LOADSTONE, Fe_3O_4, or probably $FeO+Fe_2O_3$. — A natural product, one of the most valuable of the iron ores, often found in regular octahedral crystals, which are magnetic. It may be prepared by mixing due proportions of salts of the protoxide and sesquioxide of iron, precipitating them by excess of alkali, and then boiling the mixed hydrates, when the latter unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapour. It is incapable of forming salts.

FERRIC ACID, FeO_3. — A very remarkable compound of recent discovery. The simplest mode of preparing it is to heat to full redness, for an hour, in a covered crucible, a mixture of one part of pure sesquioxide of iron, and four parts of dry nitre. The brown, porous, deliquescent mass is treated when cold with ice-cold water, by which a deep amethystine red solution of ferrate of potassa is obtained. This gradually decomposes even in the cold, evolving oxygen gas, and depositing sesquioxide; by heat the decomposition is very rapid. The solution of ferrate of potassa gives no precipitate with salts of lime, magnesia, or strontia, but when mixed with one of baryta, a deep crimson, insoluble compound falls, which is a ferrate of that base, and is very permanent.

PROTOCHLORIDE OF IRON, FeCl. — Formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the protochloride, containing 4 equivalents of water; they are very soluble and deliquescent, and rapidly oxidize in the air.

SESQUICHLORIDE OF IRON, Fe_2Cl_3. — Usually prepared by dissolving sesquioxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red, hydrated crystals, which are very soluble in water and alcohol. It forms double salts with chloride of potassium and sal-ammoniac. When evaporated to dryness and strongly heated, much of the chloride is decomposed, yielding sesquioxide and hydrochloric acid; the remainder sublimes, and afterwards condenses in the form of small brilliant red crystals, which deliquesce rapidly. The solution of sesquichloride of iron is capable of dissolving a large excess of recently precipitated hydrate of the sesquioxide, by

[1] In the form of hydrate, Fe_2O_3+3HO, as recently precipitated from the persulphate by ammonia, it constitutes the antidote for arsenious acid. The affinity for water in this case is not strong—the *hydrate gradually decomposing* even when kept under water, its colour passing from *yellowish brown to red.—R. B.*

which it acquires a much darker colour. Anhydrous sesquichloride (is also produced by the action of chlorine upon the heated metal.

PROTIODIDE OF IRON,, FeI. — This is an important medicinal prepa it is easily made by digesting iodine with water and metallic iron. 1 lution is pale green, and yields, on evaporation, crystals resembling tl the chloride, which rapidly oxidize on exposure to air. It is best pr in solution in contact with excess of iron.[1] A sesqui-iodide of iron which is yellowish-red and soluble.

SULPHIDES OF IRON. — Several compounds of iron and sulphur scribed; of these the two most important are the following. *Proton* FeS, is a blackish, brittle substance, attracted by the magnet, fori heating together iron and sulphur. It is dissolved by dilute acids wi lution of sulphuretted hydrogen gas, and is constantly employed f purpose in the laboratory, being made by projecting into a red-hot (a mixture of 2½ parts of sulphur and 4 parts of iron filings or bor cast-iron, and excluding the air as much as possible. The same su is formed when a bar of white hot-iron is brought in contact with s The *bisulphide of iron*, FeS_2, iron pyrites, is a natural product, occur rocks of all ages, and evidently formed in many cases by the grad oxidation of sulphate of iron by organic matter. It has a brass colour, is very hard, not attracted by the magnet, and not acted u dilute acids. Exposed to heat, sulphur is expelled, and an intermedi phide, analogous probably to the black oxide, is produced. This su also occurs native, under the name of *magnetic pyrites*. The bisul sometimes used in the manufacture of sulphuric acid.

Compounds of iron with phosphorus, carbon, and silicium exist, b is known respecting them in a definite state. The carbide is conta cast-iron and in steel, to which it communicates ready fusibility; the s compound is also found in cast-iron. Phosphorus is a very hurtful su in bar-iron, as it renders it brittle or *cold-short*.

SULPHATE OF PROTOXIDE OF IRON; GREEN VITRIOL, FeO,SO_3+7HC beautiful and important salt may be obtained by directly dissolving dilute sulphuric acid; it is generally prepared, however, and that o large scale, by contact of air and moisture with common iron pyrites by absorption of oxygen, readily furnishes the substance in question. of this material are exposed to the air until the decomposition is suf advanced; the salt produced is then dissolved out by water, and the made to crystallize. It forms large green crystals, of the compositic stated, which slowly effloresce and oxidize in the air; it is soluble twice its weight of cold water. Crystals containing 4, and also 2 lents of water, have been obtained. Sulphate of protoxide of iro double salts with the sulphates of potassa and ammonia.

SULPHATE OF SESQUIOXIDE OF IRON, $Fe_2O_3,3SO_3$. — Prepared by a a solution of the protosalt exactly one-half as much sulphuric ac already contains, raising the liquid to the boiling-point, and then d in nitric acid until the solution ceases to blacken by such addition. liquid thus obtained furnishes, on evaporation to dryness, a buff- amorphous mass, which, when put into water, very slowly dissolves the sulphates of potassa and ammonia, this salt yields compounds the form and constitution of the alums; the crystals are nearly des colour. These latter are decomposed by water, and sometimes by lo ing when in a dry state. They are best prepared by exposing to spo evaporation a solution of sulphate of sesquioxide of iron to which of potassa or of ammonia has been added.

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[1] Or protected from the action of oxygen by pure honey, or other saccharine in the proportion of one part to three of the solution.—R. B.

OF THE PROTOXIDE OF IRON, FeO,NO_5. — When dilute cold nitric
de to act to saturation upon protosulphide of iron, and the solu-
rated in vacuo, pale green and very soluble crystals of protonitrate
ed, which are very subject to alteration. The *nitrate* of the ses-
readily formed by pouring nitric acid, slightly diluted, upon iron;
red liquid, apt to deposit an insoluble basic salt, and is used in

ATE OF PROTOXIDE OF IRON, FeO,CO_2. — The white precipitate ob-
mixing solutions of protosalt of iron and alkaline carbonate; it
washed and dried without losing carbonic acid and absorbing
This substance occurs in nature as *spathose iron ore*, associated with
uantities of carbonate of lime and of magnesia; and also in the
'ay iron-stone, from which nearly all the British iron is made. It
und in mineral waters, being soluble in excess of carbonic acid;
rs are known by the rusty matter they deposit. No carbonate of
oxide is known.
sphates of iron are all insoluble.[1]

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the protoxide of iron are thus distinguished:—
alkalis, and ammonia, give nearly white precipitates, insoluble in
the reagent, rapidly becoming green, and ultimately brown, by ex-
air.
carbonates, and carbonate of ammonia, throw down the white
also very subject to change.
etted hydrogen gives no precipitate, but sulphide of ammonium
wn black protosulphide of iron, soluble in dilute acids.
anide of potassium gives a nearly white precipitate, becoming deep
posure to air.
the sesquioxide are thus characterized:—
alkalis, and ammonia, give foxy-red precipitates of hydrated ses-
insoluble in excess.
bonates behave in a similar manner, the carbonic acid escaping.
etted hydrogen gives a nearly white precipitate of sulphur, and
e sesquioxide to protoxide.
e of ammonium gives a black precipitate, slightly soluble in excess.
anide of potassium yields Prussian blue.
or infusion of gall-nuts strikes intense bluish-black with the
e solutions of salts of sesquioxide of iron.

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nufacture. — This most important branch of industry consists, as
cted, of two distinct parts; viz., the production from the ore of a
rbide) of iron, and the subsequent decomposition of the carbide,
nversion into pure or malleable iron.
y iron ore is found in association with coal, forming thin beds or
it consists, as already mentioned, of carbonate of iron mixed with
etimes lime and magnesia are also present. It is broken in pieces,

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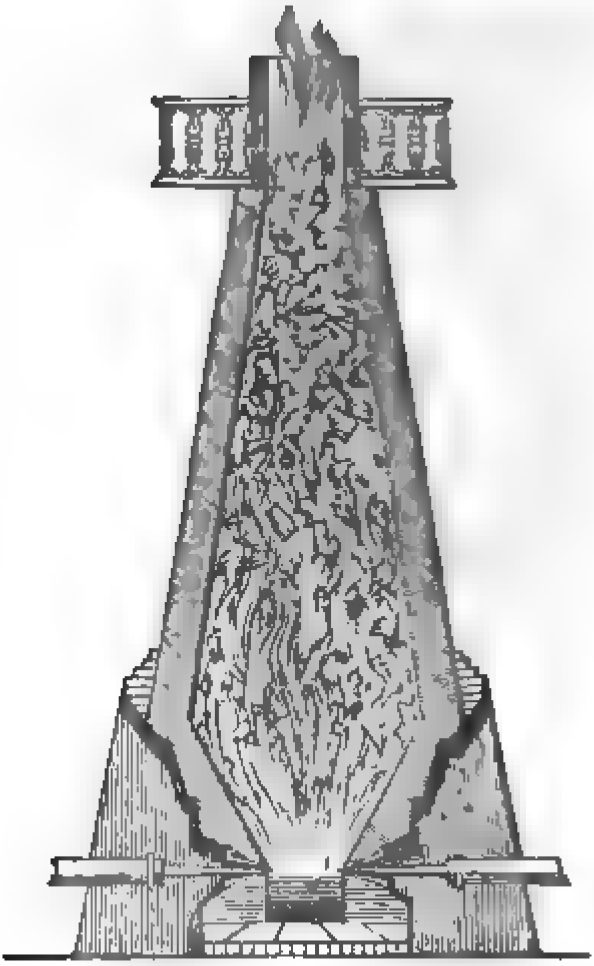
TE OF PROTOXIDE OF IRON, $2FeO, HO,PO_5$, is formed when a solution of common
f soda is added to a solution of protosulphate of iron. It falls as a white preci-
ually becoming bluish by the action of the air; it is soluble in acids, from which
ain precipitates it, and re-dissolves the precipitate when added in excess. The
ate contains perphosphate.
OF SESQUIOXIDE OF IRON is formed by adding common phosphate of soda to per-
perchloride of iron; a *white precipitate* is produced insoluble in ammonia unless
phosphate of soda be present. Digested with the fixed alkalis or ammonia it
rn.—R. B.

and exposed to heat in a furnace resembling a lime-kiln, by which the
and carbonic acid are expelled, and the ore rendered dark-coloured, d
and also magnetic; it is then ready for reduction. The furnace in
this operation is performed is usually of very large dimensions, fifty f
more in height, and constructed of brick work with great solidity
interior being lined with excellent fire-bricks: the figure will be a
understood from the sectional drawing (fig. 149). The furnace is ch

Fig. 149.



the bottom, the fire being maintained by a powerful artificial blast intr
by two or three *tuyere-pipes*, as shown in the section. The material
sisting of due proportions of coke or carbonized coal, roasted ore, an
stone, are constantly supplied from the top, the operation proceedin
tinuously night and day, often for years, or until the furnace is jud
require repair. In the upper part of the furnace, where the tempera
still very high, and where combustible gases abound, the iron of the
probably reduced to the metallic state, being disseminated throu
earthy matter of the ore; as the whole sinks down and attains a still
degree of heat, the iron becomes converted into carbide by *ceme*
while the silica and alumina unite with the lime, purposely added, to
of glass or *slag*, nearly free from oxide of iron. The carbide and sla
in a melted state, reach at last the bottom of the furnace, where they a
themselves in the order of their densities; the slag flows out at
apertures contrived for the purpose, and the iron is discharged from
time, and suffered to run into rude moulds of sand by opening an orific

' the recipient, previously stopped with clay. Such is the origin)r or cast-iron, of which there are several varieties, distinguished ıces of colour, hardness, and composition, and known by the names *lack*, and *white* iron. The first is for most purposes the best, as it being filed and cut with perfect ease. The black and grey kinds ;ontain a mechanical admixture of graphite, which separates during ion.

: improvement has been made in the above described process, by ag raw coal for coke, and blowing hot air, instead of cold, into the This is effected by causing the air, on leaving the blowing-machine, .te through a system of red-hot iron pipes, until its temperature ıigh enough to melt lead. This alteration has already effected a 3 saving in fuel, without, it appears, any injury to the quality of ct.

aversion of cast into bar-iron is effected by an operation called previous to which, however, it commonly undergoes a process the which is not perfectly intelligible. It is remelted, and suddenly which it becomes white, crystalline, and exceedingly hard: in this called *fine-metal*. The puddling process is conducted in an ordirberatory furnace, into which the charge of fine-metal is introduced aperture. This is speedily melted by the flame, and its surface ith a crust of oxide. The workman then, by the aid of an iron ently stirs the melted mass, so as intimately to mix the oxide with ; he now and then also throws in a little water, with a view of proore rapid oxidation. Small jets of blue flame soon appear upon :e of the iron, and the latter, after a time, begins to lose its fluidity, res, in succession, a pasty and a granular condition. At this point, s strongly urged, the sandy particles once more cohere, and the of the furnace now admit of being formed into several large balls , which are then withdrawn, and placed under an immense hammer, machinery, by which each becomes quickly fashioned into a rude s is re-heated, and passed between grooved cast-iron rollers, and t into a long bar or rod. To make the best iron, the bar is cut into of pieces, which are afterwards piled or bound together, again a welding heat, and hammered or rolled into a single bar; and this *piling* or *fagotting* is sometimes twice or thrice repeated, the iron greatly improved thereby.

neral nature of the change in the puddling furnace is not difficult ı. Cast-iron consists essentially of iron in combination with carbon ım; when strongly heated with oxide of iron, those compounds un;omposition, the carbon and silicium becoming oxidized at the exthe oxygen of the oxide. As this change takes place, the metal loses its fusibility, but retains a certain degree of adhesiveness, hen at last it comes under the tilt-hammer, or between the rollers, les of iron become agglutinated into a solid mass, while the readily icate of the oxide is squeezed out and separated.

se processes are, in Great Britain, performed with coal or coke, on obtained is, in many respects, inferior to that made in Sweden a from the magnetic oxide, by the use of wood charcoal, a fuel too 3 extensively employed in England. Plate-iron is, however, somele with charcoal.

A very remarkable, and most useful substance, prepared by heatin contact with charcoal. Bars of Swedish iron are embedded in powder, contained in a large rectangular crucible or chest of some capable of resisting the fire, and exposed for many hours to a full The iron takes up, under these circumstances, from 1·3 to 1·7

. . . . . . harder, and at the same time fusible, with a . . . . . malleability. The active agent in this ce- . . . . . carbonic oxide; the oxygen of the air in the . . . . . carbon, to form that substance, which is after- . . . . . heated iron, one half of its carbon being abstracted . . . . . carbonic acid thus formed takes up an additional dose . . . . . charcoal, and again becomes carbonic oxide, the oxygen, ... acting as a carrier between the charcoal and the . . . . . this operation is called blistered steel, from the blis- . . . . . appearance of the bars; the texture is afterwards improved . . . . . binding a number of these bars together, and drawing the . . . . . tilt-hammer.

. . . . . kind of steel is that which has undergone fusion, having . . . . . , and afterwards hammered: of this all fine cut- . . . . . ; it is difficult to forge, requiring great skill and . . . . . operator.

. . . . . made directly from some particular varieties of cast- . . . . . nose iron ore, containing a little manganese. The . . . . . melted state, in the hearth of a furnace, while a . . . . . on it, and causes partial oxidation: the oxide pro- . . . . . stated, on the carbon of the iron, and withdraws a . . . . . When a proper degree of stiffness or pastiness is . . . . . metal, it is withdrawn, and hammered or rolled into . . . . . tive steel of India, is probably made in this manner. . . . . . sometimes called *run-steel*, is now much employed as a . . . . . costly products of the forge; the articles, when cast, ... iron ore, or some earthy material, and, after be- . . . . . erate red-heat for some time, are allowed slowly to . . . . . extraordinary degree of softness and malleability is . . . . . that some little decarbonization may take place

. . . . . property of steel is that of becoming exceedingly . . . . . ; when heated to redness, and suddenly quenched . . . . . fact, becomes capable of scratching glass with fa- . . . . . redness, and once more left to cool slowly, it again . . . . . as ordinary iron, and, between these two conditions, ... hardness may be attained. The articles, forged into . . . . . ned in the manner described; they are then *tempered*, ... to a proper degree of annealing heat, which is often . . . . . our of the thin film of oxide which appears on the . . . . . , a temperature of about 430° (221°C), indicated by . . . . . gives the proper temper for razors; that for scissors, ... comprised between 470° (243°C) and 490° (254°C), ... dull yellow or brown tint. Swords and watch-springs . . . . . more elastic, and must be heated to 550° (288°C) or . . . . . the surface becomes deep blue. Attention to these . . . . . of less importance, as metal baths are often sub- . . . . . in this operation.

ARIDIUM.

. . . Mars, and εἶδος, appearance) from the resemblance . . . iron. Ulgren considers this as a new metal. He . . . iron from Röros, and in iron ore from Oernstolso. . . . hanging over the existence of this metal.

CHROMIUM.

Chromium is found in the state of oxide, in combination with oxide of iron, in some abundance in the Shetland Islands, and elsewhere; as chromate of lead, it constitutes a very beautiful mineral, from which it was first obtained. The metal itself is got in a half-fused condition by mixing the oxide with one-fifth of its weight of charcoal-powder, inclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace. It is hard, greyish-white, and brittle; of 5·9 specific gravity, and exceedingly difficult of fusion. Chromium is but little oxidable, being scarcely attacked by the most powerful acids; it forms at least four compounds with oxygen, corresponding to, and probably isomorphous with, those of iron.

The equivalent of chromium is 26·8; its symbol is Cr.

Protoxide of chromium, CrO.—When potassa is added to a solution of the protochloride of chromium, a brown precipitate falls, which speedily passes to deep foxy red, with disengagement of hydrogen. The protoxide, in the state of the pale greenish hydrate, is perhaps obtained when ammonia is substituted for potassa in the preceding experiment. This substance is a powerful base, forming pale blue salts, which absorb oxygen with extreme avidity. The double sulphate of protoxide of chromium and potassa contains 6 eq. of water, like the other members of the same group.

Protosesquioxide of chromium, $CrO+Cr_2O_3$, is the above brownish-red precipitate produced by the action of water, upon the protoxide. The decomposition is not complete without boiling. This oxide corresponds with the magnetic oxide of iron, and is not salifiable.

Sesquioxide of chromium, Cr_2O_3.—When chromate of mercury, prepared by mixing solutions of the nitrate of suboxide of mercury and of chromate or bichromate of potassa, is exposed to a red-heat, it is decomposed, pure sesquioxide of chromium having a fine green colour, remaining. In this state the oxide is, like alumina after ignition, insoluble in acids. From a solution of sesquioxide of chromium in potassa or soda, green gelatinous hydrated sesquioxide of chromium is separated on standing. When finely powdered and dried over sulphuric acid, its formula is Cr_2O_3+6HO. A hydrate may also be had by boiling a somewhat dilute solution of bichromate of potassa, strongly acidulated by hydrochloric acid, with small successive portions of sugar or alcohol; in the former case, carbonic acid escapes; in the latter a substance called aldehyde and acetic acid are formed, substances with which we shall become acquainted in organic chemistry, and the chromic acid of the salt becomes converted into sesquichloride of chromium, the colour of the liquid changing from red to deep green. A slight excess of ammonia precipitates the hydrate from this solution. It has a pale purplish-green colour, which becomes full green on ignition; an extraordinary shrinking of volume and sudden incandescence is observed when the hydrate is decomposed by heat. Anhydrous sesquioxide in a beautifully crystalline condition may be prepared by heating to full redness in an earthen crucible bichromate of potassa. One-half of the acid suffers decomposition, oxygen being disengaged, and oxide of chromium left. The melted mass is then treated with water, which dissolves out neutral chromate of potassa, and the oxide is, lastly, washed and dried. Sesquioxide of chromium communicates a fine green tint to glass, and is used in enamel-painting.

The sesquioxide of chromium is a feeble base, resembling, and isomorphous with, sesquioxide of iron and alumina; the salts it forms have a green or purple colour, and are said to be poisonous.

The sulphate *of sesquioxide of* chromium is prepared by dissolving the *hydrated oxide in dilute sulphuric* acid. It unites with the sulphates of po-

tassa and of ammonia, giving rise to magnificent salts which crystallize in regular octahedrons of a deep claret colour, and possess a constitution resembling that of common alum, the alumina being replaced by sesquioxide of chromium. The finest crystals of chromium alum are obtained by spontaneous evaporation, the solution being apt to be decomposed by heat.

PROTOCHLORIDE OF CHROMIUM, CrCl. The violet coloured sesquichloride of chromium, contained in a porcelain or glass tube, is heated to redness in a current of perfectly dry and pure hydrogen gas; hydrochloric acid is disengaged, and a white foliated mass is obtained, which dissolves in water with great elevation of temperature, yielding a blue solution, which, by exposure to the air, absorbs oxygen with extraordinary energy, acquiring a deep green colour, and passing into the state of oxychloride of chromium, $2Cr_2Cl_3, Cr_2O_3$. The protochloride of chromium is one of the most powerful reducing or deoxidizing agents known.

SESQUICHLORIDE OF CHROMIUM, Cr_2Cl_3.—This substance is readily obtained in the anhydrous condition by heating to redness in a porcelain tube a mixture of sesquioxide of chromium and charcoal, and passing dry chlorine gas over it. The sesquichloride sublimes, and is deposited in the cool part of the tube, in the form of beautiful crystalline plates of a pale violet colour. According to M. Péligot, it is totally insoluble in water under ordinary circumstances, even at a boiling heat. It dissolves, however, and assumes the deep green hydrated state in water containing an exceedingly minute quantity of the protochloride in solution. The hydration is marked by the evolution of much heat. This remarkable effect must probably be referred to the class of actions known at present under the name of katalysis.[1]

The salts of the sesquioxide of chromium are easily recognized.

Caustic alkalis precipitate the hydrated oxide, easily soluble in excess.

Ammonia, the same, but nearly insoluble.

Carbonates of potassa, soda, and ammonia, throw down a green precipitate of carbonate and hydrate, slightly soluble in a large excess.

Sulphuretted hydrogen causes no change.

Sulphide of ammonium precipitates the hydrate of the sesquioxide.

CHROMIC ACID, CrO_3.—Whenever sesquioxide of chromium is strongly heated with an alkali, in contact with the air, oxygen is absorbed and chromic acid generated. Chromic acid may be obtained *nearly* pure, and in a state of great beauty, by the following simple process:—100 measures of a cold saturated solution of bichromate of potassa are mixed with 1[illegible] measures of oil of vitriol, and the whole suffered to cool; the chromic acid crystallizes in brilliant crimson-red prisms. The mother-liquor is poured off, and the crystals placed upon a tile to drain, being closely covered by a glass or bell-jar.[2] Chromic acid is very deliquescent and soluble in water; the solution is instantly reduced by contact with organic matter.

Chromate of Potassa, KO,CrO_3.—This is the source of all the preparations of chromium; it is made directly from the native *chrome-iron ore*, which is a compound of the sesquioxide of chromium and protoxide of iron, analogous to *magnetic iron ore*, by calcination with nitre or with carbonate of potassa, the stone being reduced to powder, and heated for a long time with the alkali in a reverberatory furnace. The product, when treated with water, yields a yellow solution, which, by evaporation deposits anhydrous crystals of the same colour, isomorphous with sulphate of potassa. Chromate of potassa has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 60° (15°·5C).

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[1] See page 156.

[2] Mr. Warrington; Proceedings of Chem. Soc. i. 18.

Bichromate of Potassa, $KO,2CrO_3$.—When sulphuric acid is added to the preceding salt in moderate quantity, one-half of the base is removed, and the neutral chromate converted into bichromate. The new salt, of which immense quantities are manufactured for use in the arts, crystallizes by slow evaporation in beautiful red tabular crystals, derived from an oblique rhombic prism. It melts when heated, and is soluble in 10 parts of water, and the solution has an acid reaction.

Chromate of Lead, PbO,CrO_3.—On mixing solution of chromate or bichromate of potassa with nitrate or acetate of lead, a brilliant yellow precipitate falls, which is the compound in question; it is the *chrome-yellow* of the painter. When this compound is boiled with lime-water, one-half of the acid is withdrawn, and a subchromate of an orange-red colour left. The subchromate is also formed by adding chromate of lead to fused nitre, and afterwards dissolving out the soluble salts by water; the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome-colours are fixed upon cloth by the alternate application of the two solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Chromate of Silver, AgO,CrO_3.—This salt precipitates as a reddish brown powder when solutions of chromate of potassa and nitrate of silver are mixed. It dissolves in hot dilute nitric acid, and separates, on cooling, in small ruby-red platy crystals. The chromates of baryta, zinc, and mercury are insoluble; the first two are yellow, the last is brick-red.

Perchromic Acid is obtained, according to Barreswill, by mixing chromic acid with dilute binoxide of hydrogen or bichromate of potassa with a dilute but very acid solution of binoxide of barium in hydrochloric acid, when a liquid is formed of a blue colour, which is removed from the aqueous solution by ether. The composition of this very unstable compound is perhaps Cr_2O_7.

A salt of chromic acid is at once recognised by its behaviour with solutions of baryta and lead; and also by its colour and capability of furnishing, by deoxidation, the green sesquioxide of chromium.

CHLOROCHROMIC ACID, CrO_2+Cl.[1]—3 parts of bichromate of potassa and 4 parts of common salt are intimately mixed and introduced into a small glass retort; 9 parts of oil of vitriol are then added, and heat applied as long as dense red vapours arise. The product is a heavy deep red liquid resembling bromine; it is decomposed by water, with production of chromic and hydrochloric acids.

NICKEL.

Nickel is found in tolerable abundance in some of the metal-bearing veins of the Hartz mountains, and in a few other localities, chiefly as arsenide, the *kupfernickel* of mineralogists, so called from its yellowish-red colour; the word *nickel* is a term of detraction, having been applied by the old German miners to what was looked upon as a kind of false copper ore.

The artificial, or perhaps rather merely fused, product, called *speiss*, is nearly the same substance, and may be employed as a source of the nickel-salts. This metal is found in meteoric iron, as already mentioned.

Nickel is easily prepared by exposing the oxalate to a high white heat, in

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[1] If this formula be trebled, we obtain $Cr_3O_6Cl_3 = 2CrO_3,CrCl_3$, and the substance becomes a compound of 2 eq. of chromic acid and 1 eq. of terchloride of chromium. The terchloride of chromium is not known in the free state.

a crucible lined with charcoal. It is a white, malleable metal, having a density of 8·8, a high melting point, and a less degree of oxidability than iron, since it is but little attacked by dilute acids. Nickel is strongly magnetic, but loses this property when heated to 660° (349°C). This metal forms two oxides, only one of which is basic. The equivalent of nickel is 29·6; its symbol is Ni.

PROTOXIDE OF NICKEL, NiO. — This compound is prepared by heating to redness the nitrate, or by precipitating a soluble salt with caustic potassa, and washing, drying, and igniting the apple-green hydrated oxide thrown down. It is an ash-grey powder, freely soluble in acids, which it completely neutralizes, being isomorphous with magnesia, and the other members of the same group. The salts of this substance, when hydrated, have usually a beautiful green colour; in the anhydrous state they are yellow.

SESQUIOXIDE, OR PEROXIDE OF NICKEL, Ni_2O_3. — This oxide is a black insoluble substance, prepared by passing chlorine through the hydrated oxide suspended in water; chloride of nickel is formed, and the oxygen of the oxide decomposed transferred to a second portion. It is also produced when a salt of nickel is mixed with a solution of bleaching-powder. The sesquioxide is decomposed by heat, and evolves chlorine when put into hot hydrochloric acid.

CHLORIDE OF NICKEL, NiCl. — This is easily prepared by dissolving oxide or carbonate of nickel in hydrochloric acid. A green solution is obtained which furnishes crystals of the same colour, containing water. When rendered anhydrous by heat, the chloride is yellow, unless it contain cobalt, in which case it has a tint of green.

SULPHATE OF NICKEL, NiO,SO_3+7HO.—This is the most important of the salts of nickel. It forms green prismatic crystals, containing 7 equivalents of water, which require 3 parts of cold water for solution. Crystals with 6 equivalents of water have also been obtained. It forms with the sulphates of potassa and ammonia beautiful double salts, $NiO,SO_3 + KO,SO_3 + 6HO$ and $NiO,SO_3 + NH_4O, SO_3+6HO$. When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

CARBONATE OF NICKEL.—When solutions of sulphate or chloride of nickel and of carbonate of soda are mixed, a pale green precipitate falls, which is a combination of carbonate and hydrate of nickel. It is readily decomposed by heat.

Pure salts of nickel are conveniently prepared on the small scale from crude speiss or kupfernickel by the following process: — The mineral is broken into small fragments, mixed with from one-fourth to half its weight of iron-filings, and the whole dissolved in aqua regia. The solution is gently evaporated to dryness, the residue treated with boiling water, and the insoluble arsenate of iron removed by a filter. The liquid is then acidulated with hydrochloric acid, treated with sulphuretted hydrogen in excess, which precipitates the copper, and, after filtration, boiled with a little nitric acid to bring back the iron to the state of sesquioxide. To the cold and largely diluted liquid, solution of bicarbonate of soda is gradually added, by which the sesquioxide of iron may be completely separated without loss of nickel-salt. Lastly, the filtered solution, boiled with carbonate of soda in excess, yields an abundant pale green precipitate of carbonate of nickel,[1] from which all the other compounds may be prepared.

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[1] This precipitate may still contain cobalt, which can only be separated from it by very complicated processes, for which the more advanced student is referred to "Liebig and Kopp's *Annual Report*," ii. 334.

The salts of nickel are well characterized by their behaviour with reagents.

Caustic alkalis give a pale apple-green precipitate of hydrate, insoluble in excess.

Ammonia affords a similar precipitate, which is soluble in excess, with deep purplish-blue colour.

Carbonate of potassa and soda give pale green precipitates.

Carbonate of ammonia, a similar precipitate, soluble in excess, with blue colour.

Ferrocyanide of potassium gives a greenish-white precipitate.

Cyanide of potassium produces a green precipitate, which dissolves in an excess of the precipitant to an amber-coloured liquid which is re-precipitated by addition of hydrochloric acid.

Sulphuretted hydrogen occasions no change, if the nickel be in combination with a strong acid.

Sulphide of ammonium throws down black sulphide of nickel.

The chief use of nickel in the arts is in the preparation of a white alloy, sometimes called German silver, made by melting together 100 parts of copper, 60 of zinc, and 40 of nickel. This alloy is very malleable, and takes a high polish.

COBALT.

This substance bears, in many respects, an extraordinary resemblance to the metal last described; it is often associated with it in nature, and may be obtained from its compounds by similar means. Cobalt is a white, brittle metal, having a specific gravity of 8·5, and a very high melting point. It is unchanged in the air, and but feebly attacked by dilute hodrochloric and sulphuric acids. It is strongly magnetic. There are two oxides of this metal, corresponding in properties and constitution with those of nickel.

The equivalent of cobalt is 29·55: its symbol is Co.

Protoxide of cobalt, CoO.—This is a grey powder, very soluble in acids, and is a strong base, isomorphous with magnesia, affording salts of a fine red tint. It is prepared by precipitating sulphate or chloride of cobalt with carbonate of soda, and washing and drying and igniting the precipitate. When the cobalt-solution is mixed with caustic potassa a beautiful blue precipitate falls, which when heated becomes violet, and at length dirty red, from absorption of oxygen and a change in the state of hydration.

Sesquioxide of cobalt, Co_2O_3. — The sesquioxide is a black, insoluble, neutral powder, obtained by mixing solutions of cobalt and of chloride of lime.

Chloride of cobalt, $CoCl$. — The chloride is easily prepared by dissolving the oxide in hydrochloric acid; it gives a deep rose-red solution, which, when sufficiently strong, deposits hydrated crystals of the same colour. When the liquid is evaporated by heat to a very small bulk, it deposits anhydrous crystals which are blue; these latter by contact with water again dissolve to a red liquid. A dilute solution of chloride of cobalt constitutes the well-known *blue sympathetic ink;* characters written on paper with this liquid are invisible from their paleness of colour until the salt has been rendered anhydrous by exposure to heat, when the letters appear blue. When laid aside, moisture is absorbed, and the writing once more disappears. Green sympathetic ink is a mixture of the chlorides of cobalt and nickel.

Chloride of cobalt may be prepared directly from *cobalt-glance*, the native arsenide, by a process exactly similar to that described in the case of nickel.

SULPHATE OF COBALT, CoO,SO_3+7HO.—This salt forms deep red crystals, requiring for solution 24 parts of cold water; they are identical in form with those of sulphate of magnesia. It combines with the sulphates of potassa and ammonia, forming double salts, which contain as usual six equivalents of water.

A solution of oxalic acid added to one of sulphate of cobalt occasions, after some time, the separation of nearly the whole of the base in the state of oxalate.

CARBONATE OF COBALT. — The alkaline carbonates produce in solution of cobalt a pale peach-blossom coloured precipitate of combined carbonate and hydrate, containing $3(CoO,HO)+2(CoOCO_2)$.

The salts of cobalt have the following characters:—

Solution of potassa gives a blue precipitate, changing by heat to violet and red.

Ammonia gives a blue precipitate, soluble with difficulty in excess, with brownish red colour.

Carbonate of soda affords a pink precipitate.

Carbonate of ammonia, a similar compound, soluble in excess.

Ferrocyanide of potassium gives a greyish-green precipitate.

Cyanide of potassium affords a yellowish-brown precipitate, which dissolves in an excess of the precipitant. The clear solutions, after boiling, may be mixed with hydrochloric acid without giving a precipitate.

Sulphuretted hydrogen produces no change, if the cobalt be in combination with a strong acid.

Sulphide of ammonium throws down black sulphide of cobalt.

Oxide of cobalt is remarkable for the magnificent blue colour it communicates to glass: indeed this is a character by which its presence may be most easily detected, a very small portion of the substance to be examined being fused with borax on a loop of platinum wire before the blowpipe. The substance called *smalt*, used as a pigment, consists of glass coloured by oxide of cobalt; it is thus made:—The cobalt ore is roasted until nearly free from arsenic, and then fused with a mixture of carbonate of potassa and quartz-sand, free from oxide of iron. Any nickel that may happen to be contained in the ore then subsides to the bottom of the crucible as arsenide; this is the *speiss* of which mention has already been made. The glass, when complete, is removed and poured into cold water; it is afterwards ground to powder and elutriated. *Cobalt-ultramarine* is a fine blue colour prepared by mixing 16 parts of freshly precipitated alumina with 2 parts of phosphate or arsenate of cobalt: this mixture is dried and slowly heated to redness. By daylight the colour is pure blue, but by artificial light it is violet. *Zaffer* is the roasted cobalt ore mixed with a quantity of siliceous sand, and reduced to fine powder; it is used in enamel-painting. A mixture in due proportions of the oxides of cobalt, manganese, and iron is used for giving a fine black colour to glass.

ZINC.

Zinc is a somewhat abundant metal; it is found in the state of carbonate and sulphide associated with lead ores in many districts, both in Britain and

the Continent; large supplies are obtained from Silesia. The native carbonate, or *calamine*, is the most valuable of the zinc ores, and is preferred for the extraction of the metal; it is first roasted to expel water and carbonic acid, mixed with fragments of coke or charcoal, and then distilled at a full red-heat in a large earthen retort; carbonic oxide escapes, while the reduced metal volatilizes and is condensed by suitable means, generally with minute quantities of arsenic.

Zinc is a bluish-white metal, which slowly tarnishes in the air; it has a lamellar, crystalline structure, a density varying from 6·8 to 7·2, and is, under ordinary circumstances, brittle. Between 250° (121°C) and 300° (149°C) it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture, and, what is very remarkable, after such treatment, retains it malleability when cold: the sheet-zinc of commerce is thus made. At 400° (204°·4C) it is so brittle that it may be reduced to powder. At 773° (411°·6C) it melts: at a bright red-heat it boils and volatilizes, and, if air, be admitted, burns with a splendid green light, generating the oxide. Dilute acids dissolve zinc very readily; it is constantly employed in this manner in preparing hydrogen gas.

The equivalent of zinc has been fixed at 32·6; its symbol is Zn.

Protoxide of zinc, ZnO.—Only one oxide of this metal is known to exist; it is a strong base, isomorphous with magnesia; it is prepared either by burning zinc in atmospheric air, or by heating to redness the carbonate. Oxide of zinc is a white tasteless powder, insoluble in water, but freely dissolved by acids. When heated it is yellow, but turns white again on cooling.

Sulphate of zinc; white vitriol; ZnO, SO_3+7HO. This salt is hardly to be distinguished by the eye from the sulphate of magnesia; it is prepared by dissolving the metal in dilute sulphuric acid, or, more economically, by roasting the native sulphide, or *blende*, which by absorption of oxygen becomes in great part converted into sulphate of the oxide. The altered mineral is thrown hot into water, and the salt obtained by evaporating the clear solution. Sulphate of zinc has an astringent metallic taste, and is used in medicine as an emetic. The crystals dissolve in $2\frac{1}{2}$ parts of cold, and in a much smaller quantity of hot water. Crystals containing 6 equivalents of water have been observed. Sulphate of zinc forms double salts with the sulphates of potassa and ammonia.

Carbonate of zinc, ZnO,CO_2.—The neutral carbonate is found native; the white precipitate obtained by mixing solutions of zinc and of alkaline carbonates is a combination of carbonate and hydrate. When heated to redness, it yields pure oxide of zinc.

Chloride of zinc, ZnCl.—The chloride may be prepared by heating metallic zinc in chlorine; by distilling a mixture of zinc-filings and corrosive sublimate; or, more easily, by dissolving zinc in hydrochloric acid. It is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. A strong solution of chloride of zinc is sometimes used as a bath for obtaining a graduated heat above 212° (100°C). Chloride of zinc unites with sal-ammoniac and chloride of potassium to double salts; the former of these, made by dissolving an equivalent of zinc in the requisite quantity of hydrochloric acid, and then adding an equivalent of sal-ammoniac, is very useful in tinning and soft-soldering copper and iron.

A salt of zinc is easily distinguished by appropriate reagents.

Caustic potassa and soda give a white precipitate of hydrate, freely soluble in excess of alkali.

Ammonia *behaves in the same* manner; an excess re-dissolves the precipitate *instantly*.

The carbonates of potassa and soda give white precipitates, insoluble in excess.

Carbonate of ammonia gives also a white precipitate, which is re-dissolved by an excess.

Ferrocyanide of potassium gives a white precipitate.

Sulphuretted hydrogen causes no change.[1]

Sulphide of ammonium throws down white sulphide of zinc.

The applications of metallic zinc to the purposes of roofing, the construction of water-channels, &c., are well known; it is exceedingly durable, but inferior in this respect to copper.

CADMIUM.

This metal was discovered in 1817 by Stromeyer; it accompanies the ores of zinc, and, being more volatile than that substance, rises first in vapour when the calamine is subjected to distillation with charcoal. Cadmium resembles tin in colour, but is somewhat harder; it is very malleable, has a density of 8·7, melts below 500° (260°C), and is nearly as volatile as mercury. It tarnishes but little in the air, but, when strongly heated, burns. Dilute sulphuric and hydrochloric acids act but little on this metal in the cold; nitric acid is its best solvent.

The equivalent of cadmium is 56; its symbol is Cd.

PROTOXIDE OF CADMIUM, CdO. — The oxide may be prepared by igniting either the carbonate or the nitrate; in the former case it has a pale brown colour, and in the latter a much darker tint and a crystalline aspect. Oxide of cadmium is infusible; it dissolves in acids, producing a series of colourless salts.

SULPHATE OF CADMIUM, CdO,SO_3+4HO. — This is easily obtained by dissolving the oxide or carbonate in dilute sulphuric acid; it is very soluble in water, and forms double salts with the sulphates of potassa and of ammonia, which contain CdO,SO_3+KO,SO_3+6HO, and CdO,SO_3+NH_4O,SO_3+6HO.

CHLORIDE OF CADMIUM, $CdCl$. — This is a very soluble salt, crystallizing in small four-sided prisms.

SULPHIDE OF CADMIUM is a very characteristic compound, of a bright yellow colour, fusible at a high temperature. It is obtained by passing sulphuretted hydrogen gas through a solution of the sulphate, nitrate, or chloride.

The salts of cadmium are thus distinguished:—

Fixed caustic alkalis give a white precipitate of hydrated oxide, insoluble in excess.

Ammonia gives a similar white precipitate, readily soluble in excess.

The alkaline carbonates, and carbonate of ammonia, throw down white carbonate of cadmium, insoluble in excess of either precipitant.

Sulphuretted hydrogen and sulphide of ammonium precipitate the yellow sulphide of cadmium.

BISMUTH.

Bismuth is found chiefly in the metallic state, disseminated through an earthy matrix, from which it is separated by simple exposure to heat. The metal is highly crystalline and very brittle; it has a reddish-white colour, and a density of 9·9. Cubic crystals of great beauty may be obtained by

[1] With neutral solutions, or zinc-salts of an organic acid, a white precipitate ensues.

lowly cooling a considerable mass of this substance until solidification has commenced, and then piercing the crust, and pouring out the fluid residue. Bismuth melts at about 500° (260°C), and volatilizes at a high temperature: it is little oxidized by the air, but burns when strongly heated with a bluish flame. Nitric acid, somewhat diluted, dissolves it freely.

The equivalent of bismuth is 213, its symbol is Bi.

TEROXIDE OF BISMUTH, BiO_3. — This is the base of all the salts. It is a straw-yellow powder, obtained by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

BISMUTHIC ACID, BiO_5. — If teroxide of bismuth be suspended in a strong solution of potassa, and chlorine be passed through this liquid, decomposition of water ensues; hydrochloric acid being formed and the teroxide converted into the pentoxide. To separate any teroxide which may have escaped oxidation, the powder is treated with dilute nitric acid, when the bismuthic acid is left as a reddish powder, which is insoluble in water. This substance combines with bases, but the compounds are not very well known. When heated it loses oxygen, an intermediate oxide BiO_4 being formed, which may be considered as bismuthate of bismuth, $2BiO_4 = BiO_3,BiO_5$.

NITRATE OF BISMUTH, BiO_3,NO_5+9HO. — When bismuth is dissolved in moderately strong nitric acid to saturation, and the whole left to cool, large, colourless, transparent crystals of the neutral nitrate are deposited. Water decomposes these crystals; and an acid solution containing a little bismuth is obtained, and a brilliant white crystalline powder is left, which varies to a certain extent in composition according to the temperature and the quantity of water employed, but which frequently consists of a basic nitrate of the teroxide $BiO_3,3NO_5+2HO$. A solution of nitrate of bismuth, free from any great excess of acid, poured into a large quantity of cold water, yields an insoluble basic nitrate, very similar in appearance to the above, but containing rather a larger proportion of teroxide of bismuth. This remarkable decomposition illustrates at once the basic property of water, and the feeble affinity of teroxide of bismuth for acids, the nitric acid dividing itself between the two bases. The decomposition of a neutral salt by water is by no means an uncommon occurrence in the history of the metals; a solution of terchloride of antimony exhibits the same phenomenon; certain salts of mercury are affected in a similar manner, and other cases might perhaps be cited, less conspicuous, where the same change takes place to a smaller extent.

The basic nitrate of teroxide of bismuth was once extensively employed as a cosmetic, but is said to injure the skin, rendering it yellow and leather-like. It has been used in medicine.

The other salts of bismuth possess few points of interest.

Bismuth is sufficiently characterized by the decomposition of the nitrate by water, and by the blackening the nitrate undergoes when exposed to the action of sulphuretted hydrogen gas.

A mixture of 8 parts of bismuth, 5 parts of lead, and 3 of tin, is known under the name of *fusible metal*, and is employed in taking impressions from dies and for other purposes; it melts below 212° (100°C). The discrepancies so frequently observed between the properties of alloys and those of their constituent metals, plainly show that such substances must be looked upon as true chemical compounds, and not as mere mixtures; in the present case the proof is complete, for the fusible metal has lately been obtained in crystals.

URANIUM.

This metal is found in a few minerals, as *pitchblende* and *uranite*, of which the former is the most abundant. It appears from the recent interesting researches of M. Péligot, that the substance hitherto taken for metallic uranium, obtained by the action of hydrogen gas upon the black oxide, is not in reality the metal, but a protoxide, capable of uniting directly with acids, and, like the protoxide of manganese, not decomposable by hydrogen at a red-heat. The metal itself can be obtained only by the intervention of potassium, applied in the same manner as in the preparation of magnesium. It is described as a black coherent powder, or a white malleable metal, according to the state of aggregation, not oxidized by air or water, but eminently combustible when exposed to heat. It unites also with great violence with chlorine and with sulphur. M. Péligot admits three distinct oxides of uranium, besides two other compounds of the metal and oxygen, which he designates as suboxides.

The equivalent of uranium is 60. Its symbol is U.

PROTOXIDE OF URANIUM, UO.—This is the ancient metal; it is prepared by several processes, one of which has been already mentioned. It is a brown powder, sometimes highly crystalline. When in minute division it is pyrophoric, taking fire in the air, and burning to black oxide. It forms with acids a series of green salts. A corresponding chloride exists, which forms dark green octahedral crystals, highly deliquescent and soluble in water. M. Péligot attributes a very extraordinary double function to this substance, namely, that of acting as a protoxide and forming salts with acids, and that of combining with chlorine or oxygen after the fashion of an elementary body.

PROTOSESQUIOXIDE OF URANIUM; BLACK OXIDE; U_4O_5, or $2UO+U_2O_3$. The black oxide, formerly considered as protoxide, is produced when both protoxide and sesquioxide are strongly heated in the air, the former gaining, and the latter losing, a certain quantity of oxygen. It forms no salts, but is resolved by solution in acids into protoxide and sesquioxide.

SESQUIOXIDE OF URANIUM, U_2O_3.—The sesquioxide is the best known and most important of the three; it forms a number of extremely beautiful yellow salts. When caustic alkali is added to a solution of nitrate of sesquioxide of uranium, a yellow precipitate of hydrated oxide falls, which retains, however, a portion of the precipitant. The hydrate cannot be exposed to a heat sufficient to expel the water without a commencement of decomposition. A better method of obtaining the sesquioxide is to heat by means of an oil-bath the powdered and dried crystals of the nitrate to 480° (249°C), until no more nitrous fumes are disengaged. Its colour in this state is chamois-yellow.

NITRATE OF SESQUIOXIDE OF URANIUM, U_2O_3,NO_5+6HO; or $(U_2O_2)O,NO_5+6HO$; U_2O_2 being the supposed *quasi-metal*.—This nitrate is the starting point in the preparation of all the compounds of uranium; it may be prepared from pitchblende by dissolving the pulverized mineral in nitric acid, evaporating to dryness, adding water and filtering; the liquid furnishes, by due evaporation, crystals of nitrate of uranium, which are purified by a repetition of the process, and, lastly, dissolved in ether. This latter solution yields the pure nitrate.

The green salts of uranium are peroxidized by boiling with nitric acid.

A yellow precipitate with caustic alkalis, convertible by heat into black oxide; a brown precipitate with sulphide of ammonium; and none at all with sulphuretted hydrogen gas, sufficiently characterize the salts of sesqui-

oxide of uranium. A solution suspected to contain protoxide may be boiled with a little nitric acid, and then examined.

The only application of uranium is that to enamel-painting and the staining of glass; the protoxide giving a fine black colour, and the sesquioxide a delicate yellow.

COPPER.

Copper is a metal of great value in the arts of life; it sometimes occurs in the metallic state, crystallized in octahedrons, but is more abundant in the condition of red oxide, and in that of sulphide combined with sulphide of iron, or *yellow copper ore*. Large quantities of the latter substance are annually obtained from the Cornish mines and taken to South Wales for reduction, which is effected by a somewhat complex process. The principle of this may, however, be easily made intelligible. The ore is roasted in a reverberatory furnace, by which much of the sulphide of iron is converted into oxide, while the sulphide of copper remains unaltered. The product of this operation is then strongly heated with siliceous sand; the latter combines with the oxide of iron to a fusible *slag*, and separates from the heavier copper-compound. When the iron has, by a repetition of these processes been got rid of, the sulphide of copper begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen; the temperature is then raised sufficiently to reduce the oxide thus produced, by the aid of carbonaceous matter. The last part of the operation consists in thrusting into the melted metal a pole of birch-wood, the object of which is probably to reduce a little remaining oxide by the combustible gases thus generated. Large quantities of extremely valuable ore, chiefly carbonate and red oxide, have lately been obtained from South Australia.

Copper has a well-known yellowish-red colour, a specific gravity of 8·96, and is very malleable and ductile; it is an excellent conductor of heat and electricity; it melts at a bright red-heat, and seems to be a little volatile at a very high temperature. Copper undergoes no change in dry air; exposed to a moist atmosphere, it becomes covered with a strongly adherent green crust, consisting in a great measure of carbonate. Heated to redness in the air, it is quickly oxidized, becoming covered with a black scale. Dilute sulphuric and hydrochloric acids scarcely act upon copper; boiling oil of vitriol attacks it with evolution of sulphurous acid; nitric acid, even dilute, dissolves it readily with evolution of binoxide of nitrogen. Two oxides are known which form salts; a third, or peroxide, is said to exist.

The equivalent of copper is 31·7; its symbol Cu.

Protoxide of copper; black oxide; CuO.—This is the base of the ordinary blue and green salts. It is prepared by calcining metallic copper at a red-heat, with full exposure to air, or, more conveniently, by heating to redness the nitrate, which suffers complete decomposition. When a salt of this oxide is mixed with caustic alkali in excess, a bulky pale blue precipitate of hydrated oxide falls, which, when the whole is raised to the boiling-point, becomes converted into a heavy dark brown powder; this also is anhydrous oxide of copper, the hydrate suffering decomposition, even in contact with water. The oxide prepared at a high temperature is perfectly black and very dense. Protoxide of copper is soluble in acids, and forms a series of very important salts, being isomorphous with magnesia.

Suboxide of copper; red oxide; Cu_2O.—The suboxide may be obtained by heating in a covered crucible a mixture of 5 parts of black oxide and 4 parts of fine copper-filings; or by adding grape-sugar to a solution of sulphate of copper, and then putting in an excess of caustic potassa; the blue solution, heated to ebullition, is reduced by the sugar and deposits suboxide

It often occurs in beautifully transparent ruby-red crystals, associated with other ores of copper, and can be obtained in this state by artificial means. This substance forms colourless salts with acids, which are exceedingly instable, and tend to absorb oxygen. The suboxide communicates to glass a magnificent red tint, while that given by the protoxide is green.

SULPHATE OF COPPER; BLUE VITRIOL; CuO,SO_3+5HO. — This beautiful salt is prepared by dissolving oxide of copper in sulphuric acid, or, at less expense, by oxidizing the sulphide. It forms large blue crystals, soluble in 4 parts of cold and 2 of boiling water; by heat it is rendered anhydrous and nearly white, and a very high temperature decomposed. Sulphate of copper combines with the sulphates of potassa and of ammonia, forming pale blue salts which contain 6 equivalents of water, and also with ammonia, generating a remarkable compound of deep blue colour, capable of crystallizing.

NITRATE OF COPPER, CuO,NO_5+3HO. — The nitrate is easily made by dissolving the metal in nitric acid; it forms deep blue crystals, very soluble and deliquescent. It is highly corrosive. An insoluble subnitrate is known; it is green. Nitrate of copper also combines with ammonia.

CARBONATES OF COPPER. — When carbonate of soda is added in excess to a solution of sulphate of copper, the precipitate is at first pale blue and flocculent, but by warming it becomes sandy, and assumes a green tint; in this state it contains $CuO,CO_2+CuO,HO+HO$. This substance is prepared as a pigment. The beautiful mineral *malachite* has a similar composition, but contains one equivalent of water less. Another natural compound, not yet artificially imitated, occurs in large transparent crystals of the most intense blue; it contains $2(CuO,CO_2)+CuO,HO$. *Verditer*, made by decomposing nitrate of copper by chalk, is said, however, to have a somewhat similar composition.

CHLORIDE OF COPPER, $CuCl+2HO$.—The chloride is most easily prepared by dissolving the black oxide in hydrochloric acid, and concentrating the green solution thence resulting. It forms green crystals, very soluble in water and in alcohol; it colours the flame of the latter green. When gently heated, it parts with its water of crystallization and becomes yellowish-brown; at a high temperature it loses half its chlorine and becomes converted into the subchloride. The latter is a white fusible substance, but little soluble in water, and prone to oxidation; it is formed when copper-filings or copper-leaf are put into chlorine gas.

ARSENITE OF COPPER; SCHEELE'S GREEN. — This is prepared by mixing solutions of sulphate of copper and arsenite of potassa; it falls as a bright green insoluble powder.

The characters of the protosalts of copper are well marked.

Caustic of potassa gives a pale blue precipitate of hydrate, becoming blackish-brown anhydrous protoxide on boiling.

Ammonia also throws down the hydrate; but, when in excess, re-dissolves it, yielding an intense purplish blue solution.

Carbonates of potassa and soda give pale blue precipitates, insoluble in excess.

Carbonate of ammonia, the same, but soluble with deep blue colour.

Ferrocyanide of potassium gives a fine red-brown precipitate of ferrocyanide of copper.

Sulphuretted hydrogen and sulphide of ammonium afford black sulphide of copper.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added di-

y to the melted copper, or granulated copper may be heated with cala- and charcoal-powder, as in the old process. *Gun-metal*, a most worthy and valuable alloy, consists of 90 parts copper and 10 tin. *Bell* *speculum metal* contain a still larger proportion of tin; these are brittle, cially the last-named. A good bronze for statues is made of 91 parts er, 2 parts tin, 6 parts zinc, and 1 part lead. The *brass* of the ancients alloy of copper with tin.

LEAD.

is abundant and useful metal is altogether obtained from the native sul- e, or *galena*, no other lead-ore being found in quantity. The reduction is ted in a reverberatory furnace, into which the crushed lead ore is intro- d and roasted for some time at a dull red-heat, by which much of the hide becomes changed by oxidation to sulphate. The contents of the ace are then thoroughly mixed, and the temperature raised, when the hate and sulphide react upon each other, producing sulphurous acid and llic lead.[1]

ead is a soft bluish metal, possessing very little elasticity; its specific ity is 11·45. It may be easily rolled out into plates, or drawn into coarse , but has a very trifling degree of strength. Lead melts at 600° (315°·5C) little above, and at a white-heat boils and volatilizes. By slow cooling ay be obtained in octahedral crystals. In moist air this metal becomes ed with a film of grey matter, thought to be suboxide, and when exposed e atmosphere in a melted state it rapidly absorbs oxygen. Dilute acids, the exception of nitric, act but slowly upon lead. Chemists are fami- with four oxides of lead, only one of which possesses basic properties. he equivalent of lead is 103·7; its symbol is Pb.

ROTOXIDE; LITHARGE: MASSICOT; PbO. — This is the product of the ct oxidation of the metal. It is most conveniently prepared by heating carbonate to dull redness; common *litharge* is impure protoxide which undergone fusion. Protoxide of lead has a delicate straw-yellow colour, ry heavy, and slightly soluble in water, giving an alkaline liquid. At a heat it melts, and tends to crystallize on cooling. In a melted state it aks and dissolves siliceous matter with astonishing facility, often pene- ng an earthen crucible in a few minutes. It is easily reduced when ed with organic substances of any kind containing carbon or hydrogen. oxide of lead forms a large class of salts, which are colourless if the acid f be not coloured.

ED OXIDE; RED-LEAD; Pb_3O_4, or $2PbO+PbO_2$. — The composition of substance is not very constant; it is prepared by exposing for a long to the air, at a very faint red-heat, protoxide of lead which has not been l; it is a brilliant red and extremely heavy powder, decomposed with ition of oxygen by a strong heat, and converted into a mixture of pro- le and binoxide by acids. It is used as a cheap substitute for vermilion.

NOXIDE OF LEAD; PUCE OR BROWN OXIDE: PbO_2. — This compound is ned without difficulty by digesting red-lead in dilute nitric acid, when te of protoxide is dissolved out and insoluble binoxide left behind in the of a deep brown powder. The binoxide is decomposed by a red-heat, ing up one-half of its oxygen. Hydrochloric acid converts it into chlo- of lead with disengagement of chlorine; hot oil of vitriol forms with it

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[1] Sulphate of lead { Oxide of lead { Lead —— Free.
Oxygen —— 2 Sulphurous acid.
Sulphuric acid { Sulphur
3 Oxygen
Sulphide of lead .... { Sulphur
Lead —— Free.

sulphate of lead, and liberates oxygen. The binoxide is very useful in separating sulphurous acid from certain gaseous mixtures, sulphate of lead being then produced.

SUBOXIDE OF LEAD, Pb_2O.—When oxalate of lead is heated to dull redness in a retort, a grey pulverulent substance is left, which is resolved by acids into protoxide of lead and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

NITRATE OF LEAD, PbO,NO_5.—The nitrate may be obtained by dissolving carbonate of lead in nitric acid, or by acting directly upon the metal by the same agent with the aid of heat; it is, as already noticed, a by-product in the preparation of the binoxide. It crystallizes in anhydrous octahedrons, which are usually milk-white and opaque; it dissolves in 7½ parts of cold water, and is decomposed by heat, yielding nitrous acid, oxygen, and protoxide of lead, which obstinately retains traces of nitrogen. When a solution of this salt is boiled with an additional quantity of oxide of lead, a portion of the latter is dissolved, and a basic nitrate generated, which may be had in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of carbonate and hydrate of lead.

Neutral and basic compounds of oxide of lead with nitrous, and the elements of hyponitric acid, have been described. These last are probably formed by the combination of a nitrite with a nitrate.

CARBONATE OF LEAD; WHITE-LEAD; PbO,CO_2.—Carbonate of lead is sometimes found beautifully crystallized in long white needles, accompanying other metallic ores. It may be prepared by precipitating in the cold a solution of the nitrate or acetate by an alkaline carbonate; when the lead-solution is boiling, the precipitate is a basic salt, containing $2(PbO,CO_2)+HO,PbO$; it is also manufactured to an immense extent by other means for the use of the painter. Pure carbonate of lead is a soft, white powder, of great specific gravity, insoluble in water, but easily dissolved by dilute nitric or acetic acid.

Of the many methods put in practice, or proposed, for making white-lead, the two following are the most important and interesting:—One of these consists in forming a basic nitrate or acetate of lead by boiling finely powdered litharge with the neutral salt. This solution is then brought into contact with carbonic acid gas; all the excess of oxide previously taken up by the neutral salt is at once precipitated as white-lead. The solution strained or pressed from the latter is again boiled with litharge, and treated with carbonic acid, these processes being susceptible of indefinite repetition, when the little loss of neutral salt left in the precipitates is compensated. The second, and by far the more ancient method, is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which is poured a few ounces of crude vinegar; a roll of sheet-lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or, still better, spent-tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a considerable time the pile is taken down and the sheets of lead removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The nature of this curious process is generally explained by supposing the vapour of vinegar raised by the high temperature of the fermenting matter *merely to act* as a carrier between the carbonic acid evolved from the tan

and the oxide of lead formed under the influence of the acid vapour; a neutral acetate, a basic acetate, and a carbonate being produced in succession, the action gradually travelling from the surface inwards. The quantity of acetic acid used is, in relation to the lead, quite trifling, and cannot directly contribute to the production of the carbonate. A preference is still given to the product of this old mode of manufacture on account of its superiority of opacity, or *body*, over that obtained by precipitation. Commercial white-lead, however prepared, always contains a certain proportion of hydrate.

When clean metallic lead is put into pure water and exposed to the atmosphere, a white, crystalline, scaly powder begins to show itself in a few hours, and very rapidly increases in quantity. This substance may consist of hydrated protoxide of lead, formed by the action of the oxygen dissolved in the water and from the lead. It is slightly soluble, and may be readily detected in the water. In most cases, however, the formation of this deposit is due to the action of the carbonic acid dissolved in the water; it consists of carbonate in combination with hydrate, and is very insoluble in water. When common river or spring water is substituted for the pure liquid, this effect is less observable, the little sulphate, almost invariably present, causing the deposition of a very thin but closely adherent film of sulphate of lead upon the surface of the metal, which protects it from farther action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water; if the latter were quite pure, it would be speedily contaminated with lead, and the cistern be soon destroyed. Natural water highly charged with carbonic acid cannot, under any circumstances, be kept in lead, or passed through leaden pipes with safety, the carbonate, though very insoluble in pure water, being slightly soluble in water containing carbonic acid.

Chloride of lead, PbCl. — This salt is prepared by mixing strong solutions of acetate of lead and chloride of sodium; or by dissolving litharge in boiling dilute hydrochloric acid, and setting aside the filtered solution to cool. Chloride of lead crystallizes in brilliant, colourless needles, which require 135 parts of cold water for solution. It is anhydrous; it melts when heated, and solidifies on cooling to a horn-like substance.

Iodide of lead, PbI. — The iodide of lead separates as a brilliant yellow precipitate when a soluble salt of lead is mixed with iodide of potassium. This compound dissolves in boiling water, yielding a *colourless* solution, which deposits the iodide on cooling in splendid golden-yellow scales.

The soluble salts of lead thus behave with reagents:—

Caustic potassa and soda precipitate a white hydrate, freely soluble in excess.

Ammonia gives a similar white precipitate, not soluble in excess.

The carbonates of potassa, soda, and ammonia, precipitate carbonate of lead, insoluble in excess.

Sulphuric acid or a sulphate causes a white precipitate of sulphate of lead, insoluble in nitric acid.

Sulphuretted hydrogen and sulphide of ammonium throw down black sulphide of lead.

An alloy of 2 parts of lead and 1 of tin constitutes *plumber's solder;* these proportions reversed give a more fusible compound called *fine solder*. The lead employed in the manufacture of shot is combined with a little arsenic.

[1] *Ammonia gives no immediate* precipitate with the acetate.

SECTION V.

OXIDABLE METALS PROPER, WHOSE OXIDES FORM BASES OR ACIDS.

TIN.

THIS valuable metal occurs in the state of oxide, and more rarel phide; the principal tin mines are those of the Erzgebirge in Sa Bohemia, Malacca, and more especially Cornwall. In Cornwall the is found as a constituent of metal bearing veins, associated with co in granite and slate-rocks; and as an alluvial deposit, mixed with pebbles, in the beds of several small rivers. The first variety is cal and the second *stream-tin*. Oxide of tin is also found disseminated the rock itself in small crystals.

To prepare the ore for reduction, it is stamped to powder, w separate as much as possible of the earthy matter, and roasted sulphur and arsenic; it is then strongly heated with coal, and the m obtained cast into large blocks, which, after being assayed, receive t of the Duchy. Two varieties of commercial tin are known, called g *bar-tin;* the first is the best: it is prepared from the stream ore.

Pure tin has a white colour, approaching to that of silver; it is malleable, and when bent or twisted emits a peculiar crackling soun a density of 7·3 and melts at 442° (227°·77C). Tin is but little ac by air and water, even conjointly: when heated above its melting oxidizes rapidly, becoming converted into a whitish powder, used in for polishing, under the name of *putty-powder*. The metal is easily and dissolved by hydrochloric acid, with evolution of hydrogen; n acts with great energy, converting it into a white hydrate of the There are two well-marked oxides of tin, which act as feeble bases according to circumstances, and a third, which has been less studie

The equivalent of tin is 58; its symbol is Sn.

PROTOXIDE OF TIN, SnO.—When solution of protochloride of tin with carbonate of potassa, a white hydrate of the protoxide falls, bonic acid being at the same time extricated. When this is carefully dried, and heated in an atmosphere of carbonic acid, it loses wa changes to a dense black powder, which is permanent in the air, fire on the approach of a red-hot body, and burns like tinder, p binoxide. The hydrate is freely soluble in caustic potassa; the decomposes by keeping into metallic tin and binoxide.

SESQUIOXIDE OF TIN, Sn_2O_3.—The sesquioxide is produced by t of hydrated sesquioxide of iron upon protochloride of tin; it is a slimy substance, soluble in hydrochloric acid, and in ammonia. Tl has been but little examined.

BINOXIDE OF TIN, SnO_2.—This substance is obtained in two differe having properties altogether dissimilar. When bichloride of tin is tated by an alkali, a white bulky hydrate appears, which is freely

acids. If, on the other hand, the bichloride be boiled with excess of nitric acid, or if that acid be made to act directly on metallic tin, a white substance is produced, which refuses altogether to dissolve in acids, and possesses properties differing in other respects from those of the first modification. Both these varieties of binoxide of tin have the same composition, and when ignited, leave the pure binoxide of a pale lemon-yellow tint. Both dissolve in caustic alkali, and are precipitated with unchanged properties by an acid. The two hydrates redden litmus-paper.[1]

PROTOCHLORIDE OF TIN, SnCl. — The protochloride is easily made by dissolving metallic tin in hot hydrochloric acid. It crystallizes in needles containing 2 equivalents of water, which are freely soluble in a small quantity of water, but are apt to be decomposed in part when put into a large mass, unless hydrochloric acid in excess be present. The anhydrous chloride may be obtained by distilling a mixture of calomel and powdered tin, prepared by agitating the melted metal in a wooden box until it solidifies. The chloride is a grey, resinous-looking substance, fusible below redness, and volatile at a high temperature. Solution of protochloride of tin is employed as a deoxidizing agent; it reduces the salts of mercury and other metals of the same class.

BICHLORIDE OR PERCHLORIDE OF TIN, $SnCl_2$.—This is an old and very curious compound, formerly called *fuming liquor of Libavius.* It is made by exposing metallic tin to the action of chlorine, or, more conveniently, by distilling a mixture of 1 part of powdered tin, and 5 parts of corrosive sublimate. The bichloride is a thin, colourless, mobile liquid; it boils at 248° (120°C), and yields a colourless invisible vapour. It fumes in the air, and when mixed with a third part of water, solidifies to a crystalline mass. The solution of bichloride is much employed by the dyer as a *mordant;* it is commonly prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acids, care being taken to avoid too great elevation of temperature.

SULPHIDES OF TIN.—*Protosulphide*, SnS, is prepared by fusing tin with excess of sulphur, and strongly heating the product. It is a lead-grey, brittle substance, fusible by a red-heat, and soluble with evolution of sulphuretted hydrogen in hot hydrochloric acid. A *sesquisulphide* may be formed by gently heating the above compound with a third of its weight of sulphur; it is yellowish-grey, and easily decomposed by heat. *Bisulphide*, SnS_2, or *Mosaic gold*, is prepared by exposing to a low red-heat, in a glass flask, a mixture of 12 parts of tin, 6 of mercury, 6 of sal-ammoniac, and 7 of flowers of sulphur. Sal-ammoniac, cinnabar, and protochloride of tin sublime, while the bisulphide remains at the bottom of the vessel in the form of brilliant gold-coloured scales; it is used as a substitute for gold-powder.

Salts of tin are thus distinguished:—

Protoxide.

Caustic alkalis; white hydrate, soluble in excess.

Ammonia; carbonates of potassa, soda, and ammonia	White hydrate, nearly insoluble in excess.
Sulphuretted hydrogen Sulphide of ammonium	Black precipitate of protosulphide.

Binoxide.

Caustic alkalis; white hydrate, soluble in excess.
Ammonia; white hydrate, slightly soluble in excess.

[1] Fremy has called the first of these oxides stannic acid SnO_2. The second he has named metastannic acid Sn_5O_{10}. *See also H. Rose Pogg.* Ann. lxxv. 1, who thinks that there are *other modifications of this oxide of tin.*

Alkaline carbonates; white hydrates, slightly soluble in excess.
Carbonate of ammonia; white hydrate, insoluble.
Sulphuretted hydrogen; yellow precipitate of sulphide.
Sulphide of ammonium; the same, soluble in excess.

Terchloride of gold, added to a dilute solution of protochloride of tin, gives rise to a brownish-purple precipitate, called *purple of Cassius*, very characteristic, whose nature is not thoroughly understood; it is supposed to be a combination of oxide of gold and sesquioxide of tin, in which the latter acts as an acid. Heat resolves it into a mixture of metallic gold and binoxide of tin. Purple of Cassius is employed in enamel-painting.

The useful applications of tin are very numerous. *Tinned-plate* consists of iron superficially alloyed with this metal; *pewter*, of the best kind, is chiefly tin, hardened by the admixture of a little antimony, &c. Cooking vessels of copper are usually tinned in the interior.

TUNGSTEN (WOLFRAMIUM).

Tungsten is found, as tungstate of protoxide of iron, in the mineral *wolfram*, tolerable abundant in Cornwall; a native tungstate of lime is also occasionally met with. Metallic tungsten is obtained in the state of a dark grey powder, by strongly heating tungstic acid in a stream of hydrogen, but requires for fusion an exceedingly high temperature. It is a white metal very hard and brittle; it has a density of 17·4. Heated to redness in the air, it takes fire, and reproduces tungstic acid.

The equivalent of tungsten is 92, its symbol is W (wolframium).

BINOXIDE OF TUNGSTEN, WO_2. — This is most easily prepared by exposing tungstic acid to hydrogen, at a temperature which does not exceed dull redness. It is a brown powder, sometimes assuming a crystalline appearance and an imperfect metallic lustre. It takes fire when heated in the air, and burns, like the metal itself, to tungstic acid. The binoxide forms no salts with acids.

TUNGSTIC ACID, WO_3. — When tungstate of lime can be obtained, simple digestion in hot nitric acid is sufficient to remove the base, and liberate the tungstic acid in a state of tolerable purity; its extraction from wolfram, which contains tungstic acid or oxide of tungsten in association with the oxides of iron and manganese, is more difficult. Tungstic acid is a yellow powder, insoluble in water, and freely dissolved by caustic alkalis. When strongly ignited in the open air, it assumes a greenish tint.

INTERMEDIATE OR BLUE OXIDE OF TUNGSTEN, $W_2O_5, = WO_2, WO_3$.—This substance is obtained by heating tungstate of ammonia, or by exposing the brown binoxide to the action of hydrogen at a very low temperature. The same compound appears to be produced if tungstic acid be separated from one of its salts, by hydrochloric acid and the liquid be digested with metallic zinc, when the solution or the precipitate assumes a beautiful blue colour, which is very characteristic of this metal.

Two chlorides and two sulphides of tungsten are known to exist.

MOLYBDENUM.

Metallic molybdenum is obtained by exposing molybdic acid in a charcoal-lined crucible to the most intense heat that can be obtained. It is a white, brittle, and exceedingly infusible metal, having a density of 8·6, and oxidising, when heated in the air, to molybdic acid.

The equivalent of molybdenum is 46; its symbol is Mo.

PROTOXIDE OF MOLYBDENUM, MoO. — Molybdate of potassa is mixed with

excess of hydrochloric acid, by which the molybdic acid first precipitated is re-dissolved; into this acid solution zinc is put: a mixture of chloride of zinc and protochloride of molybdenum results. A large quantity of caustic potassa is then added, which precipitates a black hydrate of the protoxide of molybdenum, and retains in solution the oxide of zinc. The freshly precipitated protoxide is soluble in acids and in carbonate of ammonia; when heated in the air, it burns to binoxide.

Binoxide of molybdenum, MoO_2.—This is obtained in the anhydrous condition by heating molybdate of soda with sal-ammoniac, the molybdic acid being reduced to binoxide by the hydrogen of the ammoniacal salt; or, in a hydrated condition, by digesting metallic copper in a solution of molybdic acid in hydrochloric acid, until the liquid assumes a red colour, and then adding a large excess of ammonia. The anhydrous binoxide is deep brown, and insoluble in acids; the hydrate resembles hydrate of sesquioxide of iron, and dissolves in acids, yielding red solutions. It is converted into molybdic acid by strong nitric acid.

Molybdic acid, MoO_3.—The native bisulphide of molybdenum is roasted, at a red-heat, in an open vessel, and the impure molybdic acid thence resulting dissolved in ammonia. The filtered solution is evaporated to dryness, the salt taken up by water, and purified by crystallization. It is, lastly, decomposed by heat, and the ammonia expelled. Molybdic acid is a white crystalline powder, fusible at a red-heat, and slightly soluble in water. It is dissolved with ease by the alkalis. It forms two series of salts, namely, neutral molybdates MO,MoO_3, and acid molybdates $MO,2MoO_3$. Three chlorides, and as many sulphides of molybdenum, are described.

VANADIUM.

Vanadium is found, in small quantity, in one of the Swedish iron ores, and also as *vanadate of lead*. It has also been discovered in the iron slag of Staffordshire. The most successful process for obtaining the metal is said to be the following:—The liquid chloride of vanadium is introduced into a bulb, blown in a glass tube, and dry ammoniacal gas passed over it; the latter is absorbed, and a white saline mass produced. When this is heated by the flame of a spirit-lamp, chloride of ammonium is volatilized, and metallic vanadium left behind. It is a white brittle substance, of perfect metallic lustre, and a very high degree of infusibility; it is neither oxidized by air or water, nor attacked by sulphuric, hydrochloric, or even hydrofluoric acid; aqua regia dissolves it, yielding a deep blue solution.

The equivalent of vanadium is 68·6; its symbol is V.

Protoxide of vanadium, VO.—This is prepared by heating vanadic acid in contact with charcoal or hydrogen; it has a black colour, and imperfect metallic lustre, conducts electricity, and is very infusible. Heated in the air, it burns to binoxide. Nitric acid produces the same effect, a blue nitrate of the binoxide being generated. It does not form salts.

Binoxide of vanadium, VO_2.—The binoxide is obtained by heating a mixture of 10 parts protoxide of vanadium, and 12 of vanadic acid in a vessel filled with carbonic acid gas; or by adding a slight excess of carbonate of soda to a salt of the binoxide; in the latter case it falls as a greyish-white hydrate, readily becoming brown by absorption of oxygen. The anhydrous oxide is a black insoluble powder, convertible by heat and air into vanadic acid. It forms a series of blue salts, which have a tendency to become green and ultimately red, by the production of vanadic acid. Binoxide of vanadium also unites with alkalis.

Vanadic acid, VO_3.—The native vandate of lead is dissolved in nitric acid, and the lead and arsenic precipitated by sulphuretted hydrogen, which at the same time reduces the vanadic acid to binoxide of vanadium. The

blue filtered solution is then evaporated to dryness, and the residue digested in ammonia, which dissolves out the vanadic acid reproduced during evaporation. Into this solution a lump of sal-ammoniac is put; as that salt dissolves, vanadate of ammonia subsides as a white powder, being scarcely soluble in a saturated solution of chloride of ammonium. By exposure to a temperature below redness in an open crucible, the ammonia is expelled, and vanadic acid left. It has a dark-red colour, and melts even below a red heat; water dissolves it sparingly, and acids with greater ease; the solutions easily suffer deoxidation. It unites with bases, forming a series of yellow salts, of which those of the alkalis are soluble in water.

Chlorides of vanadium.—The *bichloride* is prepared by digesting vanadic acid in hydrochloric acid, passing a stream of sulphuretted hydrogen, and evaporating the whole to dryness. A brown residue is left, which yields a blue solution with water and an insoluble oxichloride. The *terchloride* is a yellow liquid obtained by passing chlorine over a mixture of protoxide of vanadium and charcoal. It is converted by water into hydrochloric and vanadic acids.

Two sulphides, corresponding to the chlorides, exist.

TANTALUM (COLUMBIUM).

This is an exceedingly rare substance; it is found in the minerals tantalite and *yttro-tantalite*, and may be obtained pure by heating with potassium the double fluoride of tantalum and potassium. It is a grey metal, but acted on by the ordinary acids, and burning to tantalic acid when heated in the air, or when fused with hydrate of potassa.

The equivalent of tantalum is 184; its symbol is T.

Binoxide of tantalum, TO_2.—When tantalic acid is heated to whiteness in a crucible lined with charcoal, the greater part is converted into this substance. It is a dark-brown powder, insoluble in acids, and easily changed by oxidation to tantalic acid.

Tantalic acid, TO_3.—The powdered ore is fused with three or four times its weight of carbonate of potassa, and the product digested with water; from this solution acids precipitate a white hydrate of the body in question. It is soluble in acids, but forms with them no definite compounds; with alkalis it yields, on the contrary, crystallizable salts. The specific gravity of the acid varies 7·03 to 8·26.

NIOBIUM AND PELOPIUM.

The oxides of these two metals exist in the *tantalite* of Bodenmais in Bavaria. When the supposed tantalic acid from this source is mixed with powdered charcoal, and heated to redness in a current of chlorine gas, a sublimate is obtained of a yellow, readily fusible, and very volatile substance, the chloride of *pelopium*, and a white, infusible, less volatile body, the chloride of *niobium*. The true chloride of tantalum, from the Finland tantalite, much resembles chloride of pelopium. The American tantalite contains niobic, pelopic, and tungstic acids, the former in greatest quantity.

All these chlorides are decomposed by water, with production of hydrochloric acid and the insoluble acids of the metals in the hydrated state. In properties these bodies greatly resemble each other. When heated to redness they exhibit strongly the phenomenon of incandescence. While hot, tantalic acid remains white, pelopic acid is rendered slightly yellowish and has a specific gravity varying from 5·79 to 6·37, and niobic acid becomes dark yellow, with a specific gravity between 4·56 and 5·26.

Tantalum, niobium, and pelopium may be obtained in a finely-divided *metallic state* by the action of ammonia on their respective chlorides at a high

perature. So prepared, they are black, pulverulent, not acted on by ir, but burning, when heated in the air, to acids.

TITANIUM.

rystallized oxide of titanium is found in nature in the forms of *titanite* *anatase*. Occasionally in the slag adherent to the bottom of blast-furnaces hich iron ore is reduced small brilliant copper-coloured cubes, hard igh to scratch glass, and in the highest degree infusible are found. This stance, of which a single smelting furnace in the Hartz produced as much 30 pounds, was formerly believed to be metallic titanium. Recent re-rches of Wöhler, however, have shown it to be a combination of cyanide itanium with nitride of titanium. When these crystals are powdered, ed with hydrate of potassa and fused, ammonia is evolved, and titanate otassa is formed. Metallic titanium in a finely divided state may be ob-ed by heating fluoride of titanium and potassium with potassium. There two compounds of this substance with oxygen; viz. an oxide and an l: very little is known respecting the former.

'he equivalent of titanium is 25; its symbol is Ti.

ITANIC ACID, TiO_2.—Titanate, or titaniferous iron ore, is reduced to fine rder and fused with twice its weight of carbonate of potassa, powdered, solved in dilute hydrofluoric acid when titanofluoride of titanium and assium soon begins to separate. From its hot aqueous solution snow-like nate of ammonia is precipitated by ammonia, which is easily soluble in lrochloric acid, and when ignited gives pure titanic acid. When pure the l is quite white; it is, when recently precipitated from solutions, soluble acids, but the solutions are decomposed by mere boiling. After ignition s no longer soluble, passing over into metatitanic acid. Titanic acid, on whole, very much resembles silica, and is probably often overlooked and founded with that substance in analytical researches.

ICHLORIDE OF TITANIUM.—This is a colourless, volatile liquid, resembling hloride of tin; it is obtained by passing chlorine over a mixture of titanic l and charcoal at a high temperature. It unites very violently with ter. On passing the vapour with hydrogen through a red-hot tube, lrochloric acid and a new compound Ti_2Cl_3 are formed.

ANTIMONY.

'his important metal is found chiefly in the state of sulphide. The ore is ed by fusion from earthy impurities, and is afterwards decomposed by ting with metallic iron or carbonate of potassa, which retains the sulphur. timony has a bluish-white colour and strong lustre; it is extremely ttle, being reduced to powder with the utmost ease. Its specific gravity l·8; it melts at a temperature just short of redness, and boils and vola-tes at a white-heat. This metal has always a distinct crystalline, platy cture, but by particular management it may be obtained in crystals, ich are rhombohedral. Antimony is not oxidized by the air at common peratures; strongly heated, it burns with a white flame, producing ter-de, which is often deposited in beautiful crystals. It is dissolved by hot lrochloric acid with evolution of hydrogen and production of terchloride. ric acid oxidizes it to antimonic acid, which is insoluble in that men-ruum. There are three compounds of antimony and oxygen; the first has ibtful basic properties, the second is indifferent, and the third is an acid.

'he equivalent of antimony is 129. Its symbol is Sb (stibium).

ERoxIDE OF ANTIMONY, SbO_3.—This compound may be prepared by eral methods: as by burning metallic antimony at the bottom of a large -hot crucible, in which case it is obtained in brilliant crystals; or by ring solution of terchloride of antimony into water, and digesting the

resulting precipitate with a solution of carbonate of soda. The thus produced is anhydrous; it is a pale buff-coloured powder, fu red-heat, and volatile in a close vessel, but in contact with air, it, temperature, absorbs oxygen and becomes changed to the intermedia There exists a sulphate, nitrate, and oxalate of teroxide of antimon boiled with cream of tartar (bitartrate of potassa), it is dissolved, solution yields, on evaporation, crystals of *tartar-emetic*, which is al only compound of teroxide of antimony with an acid which bears a with water without decomposition. An impure oxide for this pu sometimes prepared by carefully roasting the powdered sulphide in beratory furnace, and raising the heat at the end of the process, so a the product; it has long been known under the name of *glass of ant*

INTERMEDIATE OXIDE, $SbO_4=SbO_3,SbO_5$. — This is the ultimate of the oxidation of the metal by heat and air; it is a greyish white infusible, and destitute of volatility; it is insoluble in water and i except when recently precipitated. When treated with tartaric bitartrate of potassa, teroxide of antimony is dissolved, antimo remaining behind; alkalis, on the other hand, remove antimonic a oxide of antimony being left.

ANTIMONIC ACID, SbO_5. — When strong nitric acid is made to a metallic antimony, the metal is oxidized to its highest point, and a acid produced, which is insoluble. By exposure to a heat short of it is rendered anhydrous, and then presents the appearance of a pal coloured powder, insoluble in water and acids. It is decomposed b heat, yielding the intermediate oxide, with the loss of oxygen.

Antimonic acid is likewise obtained by decomposing pentachloride mony and an excess of water, when, together with the metallic acid acid is produced. The hydrated antimonic acid produced by the t cesses mentioned, differs in many of its properties, and especiall deportment with bases. The substance produced by nitric acid is mo producing salts of the formula MO,SbO_5. the other is bibasic, and fo series of salts of the composition $2MO,SbO_5$ and MO,HO,SbO_5. In distinguish the two modifications, M. Fremy, who first pointed out th nature of the acid obtained from the pentachloride, has proposed t guish it as metantimonic acid. Among the salts of the latter, metantimonate of potassa KO,HO,SbO_5+6HO, is to be noticed, whic a precipitate with soda-salts. It is the only reagent which precipita but must be employed with great care and circumspection. It is by fusing antimonic acid with an excess of potassa in a silver cruci solving the fused mass in a small quantity of cold water, and allow crystallize *in vacuo*. The crystals which form are metantimonate of $2KO, SbO_5$, which, when dissolved in pure water, are decomposed i potassa and acid metantimonate.

TERCHLORIDE OF ANTIMONY; BUTTER OF ANTIMONY; $SbCl_3$.—This s is produced when sulphuretted hydrogen is prepared by the action hydrochloric acid on tersulphide of antimony. The impure and hi solution thus obtained is put into a retort and distilled until each the condensed product, on falling into the aqueous liquid of the produces a copious white precipitate. The receiver is then changed, distillation continued. Pure terchloride of antimony passes over, difies on cooling to a white and highly crystalline mass, from whic requires to be carefully excluded. The same compound is formed l ling metallic antimony in powder with 2½ times its weight of corrosi mate. Terchloride of antimony is very deliquescent; it dissolves i hydrochloric acid without decomposition, and the solution poured in gives rise to a white bulky precipitate, which, after a short time

ıly crystalline, and assumes a pale fawn colour. This is the old *powder* *lgaroth;* it is a compound of terchloride and teroxide of antimony. Al-ine solutions extract the chloride and leave teroxide of antimony. Finely dered antimony thrown into chlorine gas inflames.

NTACHORIDE OF ANTIMONY, corresponding to antimonic acid, is formed passing a stream of chlorine gas ever gently heated metallic antimony; a ture of the two chlorides results, which may be separated by distillation. *pentachloride* is a colourless volatile liquid, which forms a crystalline pound with a small portion of water, but is decomposed by a larger quan-' into antimonic and hydrochloric acids.

RSULPHIDE OF ANTIMONY; CRUDE ANTIMONY; SbS_3.—The native sulphide lead-grey, brittle substance, having a radiated crystalline texture, and sily fusible. It may be prepared artificially by melting together anti-y and sulphur. When a solution of tartar-emetic is precipitated by sul-retted hydrogen, a brick-red precipitate falls, which is the same substance bined with a little water. If the precipitate be dried and gently heated, water may be expelled without other change of colour than a little dark-g, but at a higher temperature it assumes the colour and aspect of the ve sulphide. This remarkable change probably indicates a passage from amorphous to the crystalline condition.

hen powdered tersulphide of antimony is boiled in a solution of caustic ssa, it is dissolved, teroxide of antimony and sulphide of potassium being luced. The latter unites with an additional quantity of tersulphide of mony to a soluble sulphur-salt, in which the sulphide of potassium is the hur-base, and the tersulphide of antimony is the sulphur-acid.

. potassa ...	3 eq. potassium 3 eq. oxygen	3 eq. sulphide of potassium.
sulphide of imony	3 eq. sulphur 1 eq. antimony	1 eq. teroxide of antimony.

he teroxide of antimony separates in small crystals from the boiling solu-when the latter is concentrated, and the sulphur-salt dissolves an extra portion of tersulphide of antimony, which it again deposits on cooling as d amorphous powder, containing a small admixture of teroxide of anti-y and sulphide of potassium. This is the *kermes mineral* of the old mists. The filtered solution mixed with an acid gives a salt of potassa, phuretted hydrogen, and precipitated tersulphide of antimony. Kermes y also be made by fusing a mixture of 5 parts tersulphide of antimony d 8 of dry carbonate of soda, boiling the mass in 80 parts of water, and ring while hot; the compound separates on cooling.

PENTASULPHIDE OF ANTIMONY, SbS_5, formerly called *sulphur auratum*, also ts; it is a sulphur-acid. 18 parts finely powdered tersulphide of anti-y, 17 parts dry carbonate of soda, 13 parts lime in the state of hydrate, d $3\frac{1}{4}$ parts sulphur, are boiled for some hours in a quantity of water; car-ate of lime, antimonate of soda, pentasulphide of antimony, and sulphide sodium are produced. The first is insoluble, and the second partially so; two last-named bodies, on the contrary, unite to a soluble sulphur-salt, ich may by evaporation be obtained in beautiful crystals. A solution of s substance, mixed with dilute sulphuric acid, furnishes sulphate of soda, phuretted hydrogen, and pentasulphide of antimony, which falls as a lden-yellow flocculent precipitate.

ANTIMONETTED HYDROGEN.—A compound of antimony and hydrogen exists, t has not been *isolated; when* zinc is put into a solution of teroxide of timony, *and sulphuric acid* added, part of the hydrogen combines with the

antimony. This gas burns with a greenish flame, giving rise to white f of teroxide of antimony. When the gas is conducted through a red-hot tube of narrow dimensions, or burned with a limited supply of air, su is the case when a cold porcelain surface is pressed into the flame, me antimony is deposited.

The few salts of antimony soluble in water are amply characterize the orange or brick-red precipitate with sulphuretted hydrogen, whi soluble in solution of sulphide of ammonium, and again precipitated b acid.

Besides its application to medicine, antimony is of great importance in arts of life, inasmuch as it forms with lead *type-metal*. This alloy exp at the moment of solidifying, and takes an exceedingly sharp impressio the mould. It is remarkable that both its constituents shrink under sin circumstances, and make very bad castings. Tersulphide of antimony en into the composition of the blue signal-light, used at sea.[1]

TELLURIUM.

This metal, or semi-metal, is of very rare occurrence; it is found in a scarce minerals in association with silver, lead, and bismuth, appare replacing sulphur, and is most easily extracted from the sulpho-tellurid bismuth of Chemnitz, in Hungary. The finely powdered ore is mixed an equal weight of dry carbonate of soda, the mixture made into a p with oil, and heated to whiteness in a closely covered crucible. Tellu and sulphide of sodium are produced, and metallic bismuth set free. fused mass is dissolved in water and the solution freely exposed to the when the sodium and sulphur oxidize to caustic soda and hyposulphite soda, while the tellurium separates in the metallic state. Tellurium has colour and lustre of silver; by fusion and slow cooling it may be mad exhibit the form of rhombohedral crystals similar to those of antimony arsenic. It is brittle, and a comparatively bad conductor of heat and e tricity; it has a density of 6·26, melts at a little below red-heat, and v tilizes at a higher temperature. Tellurium burns when heated in the and is oxidized by nitric acid. Two compounds of this substance oxygen are known, having acid properties; they much resemble the a of arsenic.

The equivalent of tellurium is 64·2; its symbol is Te.

Tellurous acid, TeO_2.—This is obtained by burning tellurium in the or by heating it in fine powder with nitric acid of 1·25 specific gravity solution is rapidly formed, from which white anhydrous octahedral cry of tellurous acid are deposited on standing. The acid is fusible at a heat, and slightly volatile at a higher temperature; it is but feebly sol in water or acids, easily dissolved by alkalis, and reduced when heated carbon or hydrogen. A hydrate of tellurous acid is thrown down w tellurite of potassa is mixed with a slight excess of nitric acid; it is a w powder, soluble to a certain extent in water, and reddens litmus.

Telluric acid, TeO_3. — Equal parts of tellurous acid and carbonate soda are fused, and the product dissolved in water; a little hydrate of is added, and a stream of chlorine passed through the solution. The li is next saturated with ammonia, and mixed with solution of chloride barium, by which a white insoluble precipitate of tellurite of baryta is thr down. This is washed and digested with a quarter of its weight of sulph

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[1] Blue or Bengal light:—

Dry nitrate of potassa	6 parts.
Sulphur	2 "
Tersulphide of antimony	1 "

All in fine powder and intimately mixed.

id, diluted with water. The filtered solution gives, on evaporation in the ;, large crystals of telluric acid.

Telluric acid is freely, although slowly, soluble in water; it has a metallic ste, and reddens litmus-paper. When the crystals are strongly heated, ey lose water, and yield anhydrous acid, which is then insoluble in water, d even in a boiling alkaline liquid. At the temperature of ignition, telluric id loses oxygen, and passes into tellurous acid. The salts of the alkalis e soluble, but do not crystallize; those of the earths are nearly, or quite, soluble.

There are two chlorides of tellurium, and also a hydride, which closely sembles sulphuretted hydrogen.

ARSENIC.

Arsenic is sometimes found native; it occurs in considerable quantity as a stituent of many minerals, combined with metals, sulphur and oxygen. In the oxidized state it has been found in very minute quantity in a great ny mineral waters. The largest proportion is derived from the roasting f natural arsenides of iron, nickel, and cobalt; the operation is conducted a reverberatory furnace, and the volatile products condensed in a long and arly horizontal chimney, or in a kind of tower of brickwork, divided into merous chambers. The crude arsenious acid thus produced is purified by blimation, and then heated with charcoal in a retort; the metal is reduced, d readily sublimes.

Arsenic has a steel-grey colour, and high metallic lustre; it is crystalline d very brittle; it tarnishes in the air, but may be preserved unchanged in re water. Its density is 5·7 to 5·9. When heated, it volatilizes without sion, and, if air be present, oxidizes to arsenious acid. The vapour has e odour of garlic. This substance combines with metals in the same anner as sulphur and phosphorus, which it resembles, especially the latter, many respects. With oxygen it unites in two proportions, giving rise to senious and arsenic acids. There is no basic oxide of arsenic.

The equivalent of arsenic is 75; it symbol is As.

ARSENIOUS ACID; WHITE OXIDE OF ARSENIC; AsO_3.—The origin of this bstance is mentioned above. It is commonly met with in the form of a avy, white, glassy-looking substance, with smooth conchoidal fracture, hich has evidently undergone fusion. When freshly prepared, it is often ansparent, but by keeping becomes opaque, at the same time slightly minishing in density, and acquiring a greater degree of solubility in water. 00 parts of that liquid dissolve at 212° (100°C), about 11·5 parts of the paque variety; the largest portion separates, however, on cooling, leaving bout 3 parts dissolved; the solution feebly reddens litmus. Cold water, itated with powdered arsenious acid, takes up a still smaller quantity. lkalis dissolve this substance freely, forming arsenites; also compounds ith ammonia, baryta, strontia, lime, magnesia, and oxide of manganese, ave been formed; it is also easily soluble in hot hydrochloric acid. The apour of arsenious acid is colourless and inodorous; it crystallizes on solidi-ying in brilliant transparent octahedrons. The acid itself has a feeble weetish and astringent taste, and is a most fearful poison.[1]

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[1] The best antidote for arsenious acid is the hydrate of the red oxide of iron. In its recently precipitated gelatinous condition, it is most active. It acts by forming an insoluble arseniate of the protoxide of iron; for the peroxide is reduced to protoxide by losing oxygen, which, passing to the arsenious acid, forms arsenic acid. This change is represented by the following formula,

$$2\,Fe_2O_3 \text{ and } AsO_3 = 4\,FeO + AsO_5.$$

The hydrate is incapable of decomposing the arsenites. The red oxide, to act as an antidote *the arsenical salts, requires to be com*bined with an acid, which may separate the base, and

ARSENIC ACID, AsO_5.—Powdered arsenious acid is dissolved in hot hydrochloric acid, and oxidized by the addition of nitric acid, the latter being added as long as red vapours are produced; the whole is then cautiously evaporated to complete dryness. The acid thus produced is white and anhydrous. Put into water, it slowly but completely dissolves, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits, after a time, hydrated crystals of arsenic acid. When strongly heated, it is decomposed into arsenious acid and oxygen gas.

This substance is a very powerful acid, comparable with phosphoric, which it resembles in the closest manner, forming salts strictly isomorphous with the corresponding phosphates; it is also tribasic. An arsenate of soda, $2NaO,HO,AsO_5 + 24HO$, indistinguishable in appearance from common phosphate of soda, may be prepared by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallizes with 14 equivalents of water. Another arsenate, $3NaO,AsO_5 + 24HO$, is produced when carbonate of soda in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, $NaO,2HO,AsO_5 + 2HO$, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic water lose the latter at a red-heat, but unlike the phosphates, recover it when again dissolved.[1] The salts of the alkalis are soluble in water; those of the earths and other metallic oxides are insoluble, but are dissolved by acids. The precipitate with nitrate of silver is highly characteristic of arsenic acid; it is reddish-brown.

Three SULPHIDES OF ARSENIC are known. *Realgar*, AsS_2, occurs native; it is formed artificially, by heating arsenic acid with the proper proportion of sulphur. It is an orange-red, fusible, and volatile substance, employed in painting and by the pyrotechnist in making *white-fire*. *Orpiment*, AsS_3, which is also a natural product of the mineral kingdom, is made by fusing arsenic acid with excess of sulphur, or by precipitating a solution of the acid by sulphuretted hydrogen. It is a golden-yellow crystalline substance, fusible and volatile by heat. A higher sulphide, AsS_5, corresponding to arsenic acid, is produced when sulphuretted hydrogen is transmitted through a solution of arsenic acid. The solution of arsenic acid is not immediately precipitated, the pentasulphide being deposited only after some hours' standing. Its precipitation is considerably accelerated by ebullition. It is a yellow fusible substance, capable of sublimation. Realgar, orpiment, and pentasulphide of arsenic are sulphur-acids.

Arsenic unites with chlorine, iodine, &c. The *terchloride*, $AsCl_3$, is formed by distilling a mixture of 1 part of arsenic, and 6 parts of corrosive sublimate; it is a colourless, volatile liquid, decomposed by water into arsenious and hydrochloric acids. The same substance is produced, with disengagement of heat and light, when powdered arsenic is thrown into chlorine gas. The *iodide*, AsI_3, is formed by heating metallic arsenic with iodine; it is a deep red crystalline substance, capable of sublimation. The *bromide* and *fluoride* are both liquid.

Arsenic also combines with hydrogen, forming a gaseous compound, AsH_3, analogous to phosphoretted hydrogen. It is obtained pure by the action of strong hydrochloric acid on an alloy of equal parts of zinc and arsenic, and is produced in greater or less proportion whenever hydrogen is set free in

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then the arsenious acid and red oxide react on each other as above. The acetate of the red oxide is the salt used.

Magnesia has also been recommended. In the state of recently precipitated hydrate, it acts on a solution of arsenious acid with nearly the same rapidity as the hydrated peroxide of iron. In the condition usually found in the shops, it cannot be depended on with the same certainty, having been too highly calcined.—R. B.

[1] Graham, Elements, p. 435.

ntact with arsenious acid. Arsenetted hydrogen is a colourless gas, of 395 specific gravity, slightly soluble in water, and having the smell of gar-. It burns when kindled with a blue flame, generating arsenious acid. It also decomposed by transmission through a red-hot tube. Many metallic lutions are precipitated by this substance. It is, when inhaled, exceedgly poisonous, even in very minute quantity.

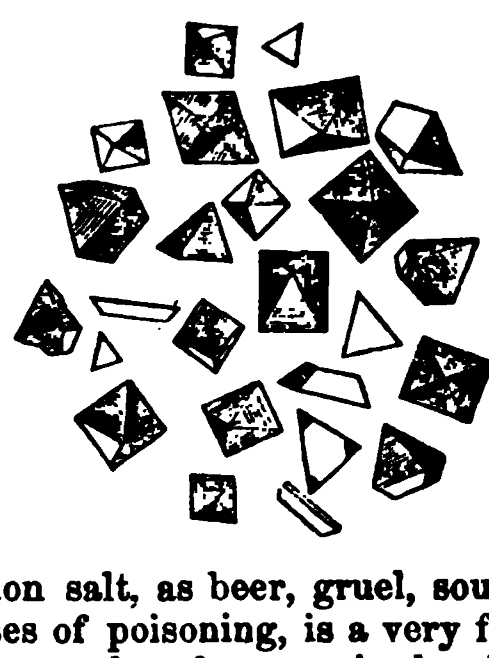
Arsenious acid is distinguished by characters which cannot be misunderood.

Nitrate of silver, mixed with a solution of arsenious acid in water, occaons no precipitate, or merely a faint cloud; but if a little alkali, as a drop ammonia, be added, a yellow precipitate of arsenite of silver immediately lls. The precipitate is exceedingly soluble in excess of ammonia; that bstance must, therefore, be added with great caution; it is likewise very luble in nitric acid.

Sulphate of copper gives no precipitation with solution of arsenious acid, ntil the addition has been made of a little alkali, when a brilliant yelloween precipitate (Scheele's green) falls, which also is very soluble in excess ammonia.

Sulphuretted hydrogen passed into a solution of arsenious acid, to which few drops of hydrochloric or sulphuric acid have been added, occasions e production of a copious bright yellow precipitate of orpiment, which is ssolved with facility by ammonia, and re-precipitated by acids.

Fig. 150.

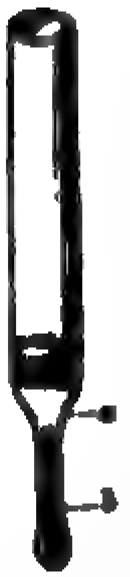


Solid arsenious acid, heated by the blowpe in a narrow glass tube with small fragents of dry charcoal, affords a sublimate metallic arsenic in the shape of a brilant steel-grey metallic ring. A portion of is, detached by the point of a knife and eated in a second glass tube, with access of r, yields, in its turn, a sublimate of colourss, transparent, octahedral crystals of arnious acid. (Fig. 150, *magnified*).

All these experiments, which *jointly* give emonstrative proof of the presence of the ubstance in question, may be performed, with erfect precision and certainty, upon exceedngly small quantities of material.

The detection of arsenious acid in complex ixtures containing organic matter and common salt, as beer, gruel, soup, &c., or the fluid contents of the stomach in cases of poisoning, is a very far ore difficult problem, but one which is, unfortunately, often required to be olved. These organic matters interfere completely with the liquid tests, nd render their indications worthless. Sometimes the difficulty may be luded by a diligent search in the suspected liquid, and in the vessel conaining it, for fragments or powder of solid arsenious acid, which, from the mall degree of solubility, often escape solution, and from the high density f the substance may be found at the bottom of the vessels in which the luids are contained. If anything of the kind be found, it may be washed y decantation with a little cold water, dried, and then reduced with charoal. For the latter purpose, a small glass tube is taken, having the figure epresented in the margin; white German glass, free from lead, is to be referred. The arsenious acid, or what is suspected to be such, is dropped o the bottom, and covered with splinters or little fragments of charcoal,

Fig. 161.

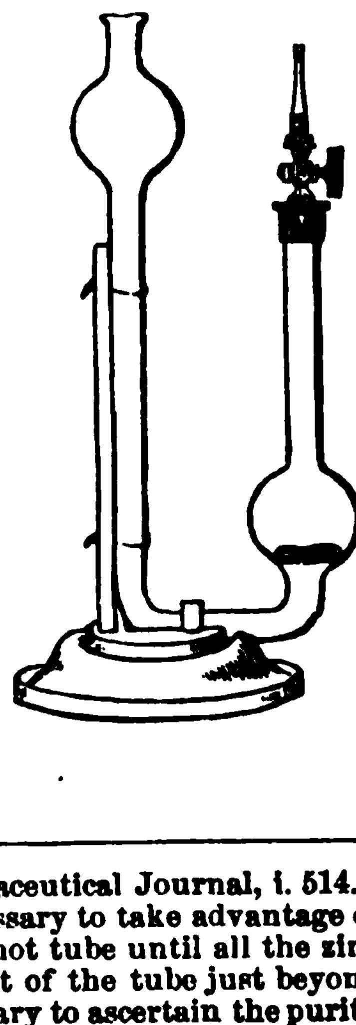


the tube being filled to the shoulder. The whole is gently heated, to expel any moisture that may be present in the charcoal, and the deposited water wiped from the interior of the tube with bibulous paper. The narrow part of the tube containing the charcoal, from *a* to *b*, (fig. 161), is now heated by the blowpipe flame; when red-hot, the tube is inclined, so that the bottom also may become heated. The arsenious acid, if present, is vaporized, and reduced by the charcoal, and a ring of metallic arsenic deposited on the cool part of the tube. To complete the experiment, the tube may be melted at *a* by the point of the flame, drawn off, and closed, and the arsenic oxidized to arsenious acid, by chasing it up and down by the heat of a small-spirit-lamp. A little water may afterwards be introduced, and boiled in the tube, by which the arsenious acid will be dissolved, and to this solution the tests of nitrate of silver and ammonia, sulphate of copper and ammonia, or sulphuretted hydrogen, may be applied.

When the search for solid arsenious acid fails, the liquid itself must be examined; a tolerably limpid solution must be obtained, from which the arsenic may be precipitated by sulphuretted hydrogen, and the orpiment collected, and reduced to the metallic state. It is in the first part of this operation that the chief difficulty is found; such organic mixtures refuse to filter, or filter so slowly as to render some method of acceleration indispensable. Boiling with a little caustic potassa or acetic acid will sometimes effect this object. The following is an outline of a plan, which has been found successful in a variety of cases, in which a very small quantity of arsenious acid had been purposely added to an organic mixture. Oil of vitriol, itself perfectly free from arsenic, is mixed with the suspected liquid, in the proportion of about a measured ounce to a pint, having been previously diluted with a little water, and the whole is boiled in a flask for half an hour, or until a complete separation of solid and liquid matter becomes manifest. The acid converts any starch that may be present into dextrin and sugar; it coagulates completely albuminous substances, and casein, in the case of milk, and brings the whole in a very short time into a state in which filtration is both easy and rapid. Through the filtered solution, when cold, a current of sulphuretted hydrogen is transmitted, and the liquid is warmed to facilitate the deposition of the tersulphide, which falls in combination with a large quantity of organic matter, which often communicates to it a dirty colour. This is collected upon a small filter, and washed. It is next transferred to a capsule, and heated with a mixture of nitric and hydrochloric acids, by which the organic impurities are in a great measure destroyed, and the arsenic oxidized to arsenic acid. The solution is evaporated to dryness, the soluble part taken up by dilute hydrochloric acid, and the the solution saturated with sulphurous acid, whereby the arsenic acid is reduced to the state of arsenious acid, the sulphurous being oxidized to sulphuric acid; the solution of arsenious acid may be precipitated by sulphuretted hydrogen without any difficulty. The liquid is warmed, and the precipitate washed by decantation, and dried. It is then mixed with *black flux*, and heated in a small glass tube, similar to that already described, with similar precautions; a ring of reduced arsenic is obtained, which may be oxidized to arsenious acid, and farther examined. The black-flux is a mixture of carbonate of potassa and charcoal, obtained by calcining cream of tartar in a close crucible; the alkali transforms the sulphide into arsenious acid, the charcoal subsequently effecting the deoxidation. A mixture of

ıs carbonate of soda and charcoal may be substituted with advan-
the common black-flux, as it is less hygroscopic.[1]
methods of proceeding, different in principle from the foregoing,
ɔn proposed, as that of the late Mr. Marsh, which is exceedingly
The suspected liquid is acidulated with sulphuric acid and placed
ɔt with metallic zinc; the hydrogen reduces the arsenious acid and
s with the arsenic, if any be present. The gas is burned at a jet,
ece of glass or porcelain held in the flame, when any admixture of
ɔd hydrogen is at once known by the production of a brilliant black
spot of reduced arsenic on the porcelain.
been observed (page 290) that antimonetted hydrogen gives a simi-
lt. In order to distinguish the two substances, the gas may be
ıto a solution of nitrate of silver. Both gases give rise to a black
ıte, which in the case of antimonetted hydrogen consists of antimo-
silver, Ag_3 Sb, whilst it is pure silver in the case of arsenetted hy-
the arsenic being then converted into arsenious acid, which combines
ɔortion of oxide of silver. The arsenite of
mains dissolved in the nitric acid which is li-
by the precipitation of the silver, and may
ɱn down with its characteristic yellow colour
g ammonia to the liquid filtered off from the
ecipitate.
venient form of Marsh's instrument is that
ı fig. 152, it consists of a bent tube, having
ɔs blown upon it, fitted with a stop-cock and
et. Slips of zinc are put into the lower bulb,
ı afterwards filled with the liquid to be ex-
On replacing the stop-cock, closed, the gas
and forces the fluid into the upper bulb,
ıen acts by its hydrostatic pressure and ex-
gas through the jet as soon as the stop-cock is
It must be borne in mind that both common
sulphuric acid often contain traces of arsenic.[2]
of copper foil boiled in the poisoned liquid,
ly acidulated with hydrochloric acid, with-
ıe arsenic and becomes covered with a white
By heating the metal in a glass tube, the
is expelled, and oxidized to arsenious acid.

Fig. 152.



ɔaper by the author on the detection of arsenic. Pharmaceutical Journal, i. 514.
e the amount of arsenic present is small, it becomes necessary to take advantage of
ı of heat, and cause the gas to pass slowly through a red-hot tube until all the zinc
d. The reduced arsenic will be deposited on the cool part of the tube just beyond
l portion. In all cases of using the above test, it is necessary to ascertain the purity
e and acid by trial, previous to addition of the suspected liquid.—R. B.

SECTION VI.

METALS WHOSE OXIDES ARE REDUCED BY HEAT.

SILVER.

Silver is found in the metallic state, in union with sulphur, and also as chloride and bromide. Among the principal silver mines may be mentioned those of the Hartz mountains in Germany, of Kongsberg in Norway, and, more particularly, of the Andes in both North and South America.

The greater part of the silver of commerce is extracted from ores so poor as to render any process of *smelting* or fusion inapplicable, even where fuel could be obtained, and this is often difficult to be procured. Recourse, therefore, is had to another method, that of *amalgamation*, founded on the easy solubility of silver and many other metals in metallic mercury.

The amalgamation-process, as conducted in Germany, differs somewhat from that in use in America. The ore is crushed to powder, mixed with a quantity of common salt, and roasted at a low red-heat in a suitable furnace, by which treatment any sulphide of silver it may contain is converted into chloride. The mixture of earthy matter, oxides of iron, copper, soluble salts, chloride of silver, and metallic silver, is sifted and put into large barrels, made to revolve on axes, with a quantity of water and scraps of iron, and the whole agitated together for some time, during which the iron reduces the chloride of silver to the state of metal. A certain proportion of mercury is then introduced, and the agitation repeated; the mercury dissolves out the silver, together with gold, if there be any, metallic copper, and other substances, forming a fluid amalgam easily separable from the thin mud of earthy matter by subsidence and washing. This amalgam is strained through strong linen cloth, and the solid portion exposed to heat in a kind of retort, by which the remaining mercury is distilled off and the silver left behind in an impure condition.

A considerable quantity of silver is obtained from argentiferous galena; in fact, almost every specimen of native sulphide of lead will be found to contain traces of this metal. When the proportion rises to a certain amount it becomes worth extracting. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then re-melted in a large vessel, and allowed slowly to cool until solidification commences. The portion which first crystallizes is nearly pure lead, the alloy with silver being *more fusible than lead itself;* by particular management this is drained away, and found to contain nearly the whole of the silver. This rich mass is next exposed to a red-heat on the shallow hearth of a furnace, while a stream of air is allowed to impinge upon its surface; oxidation takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast. When the greater part of the lead has been thus removed, the residue is transferred to a cupel or shallow dish made of bone-ashes, and again heated; the last of the lead is now oxidized, and the oxide

ks in a melted state into the porous vessel, while the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind.

Pure silver may be easily obtained. The metal is dissolved in nitric acid; t contains copper, the solution will have a blue tint; gold will remain unsolved as a black powder. The solution is mixed with hydrochloric acid with common salt, and the white, insoluble curdy precipitate of chloride silver washed and dried. This is then mixed with about twice its weight anhydrous carbonate of soda, and the mixture, placed in an earthen crule, gradually raised to a temperature approaching whiteness, during ich the carbonate of soda and the chloride react upon each other, carbonic d and oxygen escape, while metallic silver and chloride of sodium result; former fuses into a button at the bottom of the crucible, and is easily ached.

Pure silver has a most perfect white colour, and a high degree of lustre; s exceedingly malleable and ductile, and is probably the best conductor h of heat and electricity known. Its specific gravity is 10·5. In hardness les between gold and copper. It melts at a bright red-heat, about 1873° 23°C), according to the observations of Mr. Daniell. Silver is inalterable air and moisture; it refuses to oxidize at any temperature, but possesses extraordinary faculty, already noticed in an earlier part of the work, of orbing many times its volume of oxygen when strongly heated in an atsphere of that gas, or in common air. This oxygen is again disengaged the moment of solidification, and gives rise to the peculiar arborescent pearance often remarked on the surface of masses or buttons of pure ver. The addition of 2 per cent. of copper is sufficient to prevent this orption of oxygen. Silver oxidizes when heated with fusible siliceous tter, as glass, which it stains yellow or orange, from the formation of a ate. It is little attacked by hydrochloric acid; boiling oil of vitriol conts it into sulphate with evolution of sulphurous acid; and nitric acid, n dilute and in the cold, dissolves it readily. The tarnishing of surfaces silver exposed to the air is due to sulphuretted hydrogen, the metal having strong attraction for sulphur. There are three oxides of silver, one of ich is a powerful base isomorphous with potassa, soda, and oxide of ammium.

The equivalent of silver is 108; its symbol is Ag (argentum).

Suboxide of silver, Ag_2O.—When dry citrate of silver is heated to 212° 0°C) in a stream of hydrogen gas, it loses oxygen and becomes dark wn. The product dissolved in water, gives a dark-coloured solution conning free citric acid and citrate of the suboxide of silver. The suboxide then precipitated by potassa. It is a black powder, very easily decomsed, and soluble in ammonia. The solution of citrate is rendered colourless heat, being resolved into a salt of the protoxide and metallic silver.

Protoxide of silver, AgO. — Caustic potassa added to a solution of rate of silver throws down a pale-brown precipitate, which consists of toxide of silver. It is very soluble in ammonia, and is dissolved also to mall extent by pure water; the solution is alkaline. Recently precipitated loride of silver, boiled in a solution of caustic potassa of specific gravity 5, according to the observation of Dr. Gregory, is converted, although th difficulty, into oxide of silver, which in this case is black and very dense. e protoxide of silver neutralizes acids completely, and forms, for the most rt, colourless salts. It is decomposed by a red-heat, with extrication of ygen, spongy metallic silver being left; the sun's rays also effect its deposition to a small extent.

Peroxide of silver. — *This is a* black crystalline substance which forms *on the positive electrode of a* voltaic arrangement employed to decompose *lution of nitrate of silver. It is* reduced by heat, evolves chlorine when

acted upon by hydrochloric acid, explodes when mixed with phosphorus and struck, and decomposes solution of ammonia with great energy and rapid disengagement of nitrogen gas.

NITRATE OF SILVER, AgO,NO_5.—The nitrate is prepared by directly dissolving silver in nitric acid and evaporating the solution to dryness, or until it is strong enough to crystallize on cooling. The crystals are colourless, transparent, anhydrous tables, soluble in an equal weight of cold, and in half that quantity of boiling water; they also dissolve in alcohol. They fuse when heated like those of nitre, and at a higher temperature suffer decomposition; the *lunar caustic* of the surgeon is nitrate of silver which has been melted and poured into a cylindrical mould. The salt blackens when exposed to light, more particularly if organic matters of any kind be present, and is frequently employed to communicate a dark stain to the hair; it enters into the composition of the "indelible" ink used for marking linen. The black stain has been thought to be metallic silver; it may possibly be suboxide. Pure nitrate of silver may be prepared from the metal alloyed with copper: the alloy is dissolved in nitric acid, the solution evaporated to dryness, and the mixed nitrates cautiously heated to fusion. A small portion of the melted mass is removed from time to time for examination; it is dissolved in water, filtered, and ammonia added to it in excess. While any copper-salt remains undecomposed, the liquid will be blue, but when that no longer happens, the nitrate may be suffered to cool, dissolved in water, and filtered from the insoluble black oxide of copper.

SULPHATE OF SILVER, AgO,SO_3. — The sulphate may be prepared by boiling together oil of vitriol and metallic silver, or by precipitating a concentrated solution of nitrate of silver by an alkaline sulphate. It dissolves in 88 parts of boiling water, and separates in great measure in a crystalline form on cooling, having but a feeble degree of solubility at a low temperature. It forms a crystallizable compound with ammonia, freely soluble in water, containing AgO,SO_3+2NH_3.

Hyposulphate of Silver, AgO,S_2O_5+HO, is a soluble crystallizable salt, permanent in the air. The *hyposulphite* is insoluble, white, and very prone to decomposition; it combines with the alkaline hyposulphites, forming soluble compounds distinguished by an intensely sweet taste. The alkaline hyposulphites dissolve both oxide and chloride of silver, and give rise to similar salts, an oxide or chloride of the alkaline metal being at the same time formed. *Carbonate of silver* is a white insoluble substance obtained by mixing solutions of nitrate of silver and of carbonate of soda. It is blackened and decomposed by boiling.

CHLORIDE OF SILVER, $AgCl$.—This substance is almost invariably produced when a soluble salt of silver and a soluble chloride are mixed. It falls as a white curdy precipitate, quite insoluble in water and nitric acid, but one part of chloride of silver is soluble in 200 parts of hydrochloric acid when concentrated, and in about 600 parts when diluted with double its weight of water. When heated it melts, and on cooling becomes a greyish crystalline mass, which cuts like horn: it is found native in this condition, constituting the *horn-silver* of the mineralogist. Chloride of silver is decomposed by light both in a dry and wet state, *very* slowly if pure, and quickly if organic matter be present: it is reduced also when put into water with metallic zinc or iron. It is soluble with great ease in ammonia and in a solution of cyanide of potassium. In practical analysis the proportion of chlorine or hydrochloric acid in a compound is always estimated by precipitation by solution of silver. The liquid is acidulated with nitric acid, and an excess of nitrate of silver added: the chloride is collected on a filter, or better by subsidence, washed, dried, and fused; 100 parts correspond to 24·7 of chlorine, or 25·43 of hydrochloric acid.

OF SILVER, AgI. — The iodide is a pale yellow insoluble precipitate by adding nitrate of silver to iodide of potassium; it is insoluble, so, in ammonia, and forms an exception to the silver-salts in gene-his respect. The *bromide* of silver very closely resembles the

IDE OF SILVER, AgS.—This is a soft, grey, and somewhat malleable e, found native in a crystallized state, and easily produced by melt-her its constituents, or by precipitating a solution of silver by sul-l hydrogen. It is a strong sulphur-base, and combines with the of antimony and arsenic: examples of such compounds are found autiful minerals *dark* and *light red silver ore.*

IIA COMPOUND OF SILVER; BERTHOLLET'S FULMINATING SILVER.— ecipitated oxide of silver is digested in ammonia, a black substance ced, possessing exceedingly dangerous explosive properties. It while moist when rubbed with a hard body, but when dry the touch her is sufficient. The ammonia retains some of this substance in and deposits it in small crystals by spontaneous evaporation. A ompound containing oxide of gold exists. It is easy to understand n why these bodies are subject to such violent and sudden decom-by the slightest cause, on the supposition that they contain an oxide ily reducible metal and ammonia; the attraction between the two nts of the substance is very feeble, while that between the oxygen e and the hydrogen of the other is very powerful. The explosion by the sudden evolution of nitrogen gas and vapour of water, the ng set free.

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ble salt of silver is perfectly characterized by the white curdy pre-f chloride of silver, darkening by exposure to light, and insoluble tric acid, which is produced by the addition of any soluble chlo-ad is the only metal which can be confounded with it in this re-t chloride of lead is soluble to a great extent in boiling water, and ed in brilliant acicular crystals when the solution cools. Solutions are reduced to the metallic state by iron, copper, mercury, and other

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onomical uses of silver are many: it is admirable for culinary and ilar purposes, not being attacked in the slightest degree by any ibstances used for food. It is necessary, however, in these cases sh the softness of the metal by a small addition of copper. The silver of England contains 222 parts of silver and 18 parts of

GOLD.

n small quantities, is a very widely diffused metal; traces are con-und in the iron pyrites of the more ancient rocks. It is always in the metallic state, sometimes beautifully crystallized in the cubic ociated with quartz, oxide of iron, and other substances, in regular eins. The sands of various rivers have long furnished gold derived source, and separable by a simple process of washing; such is the of commerce. When a veinstone is wrought for gold, it is stamped r, and shaken in a suitable apparatus with water and mercury; an is formed, which is afterwards separated from the mixture and de-by distillation.

re metal is obtained by solution in nitro-hydrochloric acid and pre-*by a salt of protoxide* of iron, which, by undergoing peroxidation,

reduces the gold. The latter falls as a brown powder, which acquires the metallic lustre by *friction*.

Gold is a soft metal, having a beautiful yellow colour. It surpasses all other metals in malleability, the thinnest gold-leaf not exceeding, it is said, $\frac{1}{200000}$ of an inch in thickness, while the gilding on the silver wire used in the manufacture of *gold-lace* is still thinner. It may also be drawn into very fine wire. Gold has a density of 19·5; it melts at a temperature a little above the fusing-point of silver. Neither air nor water affect it in the least at any temperature; the ordinary acids fail to attack it, singly. A mixture of nitric and hydrochloric acids dissolves gold, however, with ease, the active agent being the liberated chlorine. Gold forms two compounds with oxygen, and two corresponding compounds with chlorine, iodine, sulphur, &c. Both oxides refuse to unite with acids.

The equivalent of gold is 197. Its symbol is Au (aurum).

Protoxide of gold, AuO. — The protoxide is produced when caustic potassa in solution is poured upon the protochloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold, which subsides, and into teroxide, which remains dissolved.

Teroxide of gold; auric acid; AuO_3. — When magnesia is added to the terchloride of gold, and the sparingly soluble aurate of that base well washed and digested with nitric acid, the teroxide is left as an insoluble reddish-yellow powder, which, when dry, becomes chestnut-brown. It is easily reduced by heat, and also by mere exposure to light; it is insoluble in oxygen acids with the exception of strong nitric acid, insoluble in hydrofluoric acid, easily dissolved by hydrochloric and hydrobromic acids. Alkalis dissolve it freely; indeed, the acid properties of this substance are very strongly marked; it partially decomposes a solution of chloride of potassium when boiled with that liquid, potassa being produced. When digested with ammonia, it furnishes fulminating gold.

Protochloride of gold, $AuCl$. — This substance is produced when the terchloride is evaporated to dryness and exposed to a heat of 440° (226°·6C) until chlorine ceases to be exhaled. It forms a yellowish-white mass, insoluble in water. In contact with that liquid it is decomposed slowly in the cold, and rapidly by the aid of heat, into metallic gold and terchloride.

Terchloride of gold, $AuCl_3$. — This is the most important compound of the metal; it is always produced when gold is dissolved in nitro-hydrochloric acid. The deep yellow solution thus obtained yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen; when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling, solidifies to a red crystalline mass of terchloride of gold, very deliquescent, and soluble in water, alcohol, and ether. The terchloride of gold combines with a number of metallic chlorides, forming a series of double salts, of which the general formula in the anhydrous state is $MCl + AuCl_3$, M representing an equivalent of the second metal. These compounds are mostly yellow when in crystals, and red when deprived of water.

A mixture of terchloride of gold with excess of bicarbonate of potassa or soda is used for gilding small ornamental articles of copper; these are cleaned by dilute nitric acid, and then boiled in the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

The other compounds of gold are of very little importance.

The presence of this metal in solution may be known by the brown precipitate with sulphate of protoxide of iron, fusible before the blowpipe into *a bead of gold*; and by the purple compound formed when the terchloride of gold is added to a solution of protochloride of tin.

tended for coin, and most other purposes, is always alloyed with a oportion of silver or copper, to increase its hardness and durability; amed metal confers a pale greenish colour. English standard gold $\frac{1}{12}$ of alloy, now always copper. *Gold-leaf* is made by rolling out pure gold as thin as possible, and then beating them between folds 'ane by a heavy hammer, until the requisite degree of tenuity has hed. The leaf is made to adhere to wood, &c., by size or varnish. on copper has very generally been performed by dipping the arti- a solution of nitrate of mercury, and then shaking them with a :p of a soft amalgam of gold with that metal, which thus becomes er their surfaces; the articles are subsequently heated to expel the and then burnished. Gilding on steel is done either by applying a f terchloride of gold, in ether, or by roughening the surface of the ating it, and applying gold-leaf, with a burnisher. Gilding by is—an elegant and simple method, now rapidly superseding many ers—has already been noticed. The solution usually employed is by dissolving oxide or cyanide of gold in a solution of cyanide of ı.[1]

MERCURY, OR QUICKSILVER.

ry remarkable metal has been known from an early period, and, nore than all others, has excited the attention and curiosity of ex- ers, by reason of its peculiar physical properties. Mercury is of ortance in several of the arts, and enters into the composition of uable medicaments.

c mercury is occasionally met with in globules disseminated through 'e sulphide, which is the ordinary ore. This latter substance, s called *cinnabar*, is found in considerable quantity in several of which the most celebrated are Almaden in New Castile and Carniola. Only recently it has been discovered in great abundance, markable purity, in California. The metal is obtained by heating ide in an iron retort with lime or scraps of iron, or by roasting it ace, and conducting the vapours into a large chamber, where the is condensed, while the sulphurous acid is allowed to escape. is imported into this country in bottles of hammered iron, contain- ty-five pounds each, and in a state of considerable purity. When d in smaller quantities, it is sometimes found adulterated with tin , which metals it dissolves to some extent without much loss of Such admixture may be known by the foul surface the mercury when shaken in a bottle containing air, and by the globules, when roll upon the table, having a train or tail.

ry has a nearly silver-white colour, and a very high degree of lustre; id at all ordinary temperatures, and only solidifies when cooled to $-40°C$). In this state it is soft and malleable. At 662° (350°C) it l yields a transparent, colourless vapour, of great density. The atilizes, however, to a sensible extent at all temperatures above 68° · 70° (21°C); below this point its volatility is imperceptible. The of mercury at the boiling heat is singularly retarded by the pre- minute quantities of lead or zinc. The specific gravity of mercury 5°·5C) is 13·59; that of frozen mercury about 14, great contraction ace in the act of solidification.

uicksilver is quite inalterable in the air at common temperatures, ı heated to near its boiling point it slowly absorbs oxygen, and be- nverted into a crystalline dark red powder, which is the highest

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[1] *Messrs. Elkington*, Application of Electro-Metallurgy to the Arts.

oxide. At a dull red-heat this oxide is again decomposed into its elements. Hydrochloric acid has little or no action on mercury, and the same may be said of sulphuric acid in a diluted state; when the latter is concentrated and boiling hot, it oxidizes the metal, converting it into sulphate of the red oxide, with evolution of sulphurous acid. Nitric acid, even dilute and in the cold, dissolves mercury freely, with an evolution of binoxide of nitrogen.

Mercury combines with oxygen in two proportions, forming a grey and a red oxide, both of which are salifiable. As the salts of the red oxide are the most stable and permanent, that substance may be regarded as the true protoxide, instead of the grey oxide, to which the term has formerly been applied. Until, however, isomorphous relations connecting mercury with the other metals shall be established, the constitution of the two oxides, and that of the corresponding chlorides, iodides, &c., must remain somewhat unsettled.[1]

The equivalent of mercury on the above supposition, will be 100; its symbol is Hg (hydrargyrum).

SUBOXIDE OF MERCURY; GREY OXIDE; Hg_2O.—The suboxide is easily prepared by adding caustic potassa to the nitrate of this substance, or by digesting calomel in solution of caustic alkali. It is a dark grey, nearly black, heavy powder, insoluble in water. It is slowly decomposed by the action of light into metallic mercury and red oxide. The preparations known in pharmacy by the names *blue pill*, *grey ointment*, *mercury with chalk*, &c., often supposed to owe their efficacy to this substance, merely contain finely divided metal.

PROTOXIDE OF MERCURY; RED OXIDE; HgO.—There are numerous methods by which this method may be obtained; the following may be cited as the most important:—(1) By exposing mercury in a glass flask, with a long narrow neck, for several weeks to a temperature approaching 600° (315°·5); the product has a dark red colour and is highly crystalline; it is the red *precipitate* of the old writers. (2) By cautiously heating any of the nitrates of either oxide to complete decomposition, when the acid is decomposed and expelled, oxidizing the metal to a maximum, if it happen to be in the condition of a suboxide. The product is in this case also crystalline and very dense, but has a much paler colour than the preceding; while hot it is nearly black. It is by this method that the oxide is generally prepared; it is apt to contain undecomposed nitrate, which may be discovered by strongly heating a portion in a test-tube: if red fumes are produced or the odour of nitrous acid exhaled, the oxide has been insufficiently heated in the process of manufacture. (3) By adding caustic potassa in excess to a solution of corrosive sublimate, by which a bright yellow precipitate of oxide is thrown down, which only differs from the foregoing preparations in being destitute of crystalline texture and much more minutely divided.[2] It must be well washed and dried.

Red oxide of mercury is slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste; it is highly poisonous. When strongly heated, it is decomposed, as before observed, into metallic mercury and oxygen gas.

NITRATES OF THE OXIDES OF MERCURY.—Nitric acid varies in its action upon mercury, according to the temperature. When cold and somewhat diluted, only salts of the grey oxide are formed, and these are neutral or

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[1] By referring to cyanogen, it will be perceived that when the equivalent of mercury is considered to be 100, the constitution of the cyanide of mercury is analogous to the other metallic cyanides, but when taken at 200, it becomes a bicyanide, and then differs from all others.—R. B.

[2] *This precipitate* is considered by Shauffner to be a hydrate, HgO,3HO, for by exposure to *the temperature of* 392°, it loses water amounting to over 20 per cent. of its weight.—R. B.

sic (*i. e.* with excess of oxide), as the acid or the metal happens to be in cess. When, on the contrary, the nitric acid is concentrated and hot, the rcury is raised to its highest state of oxidation, and a salt of the red oxide oduced. Both classes of salts are apt to be decomposed by a large antity of water, giving rise to insoluble, or sparingly soluble, compounds ntaining an excess of base.

Neutral nitrate of the suboxide, Hg_2O,NO_5+2HO, forms large colourless ystals, soluble in a small quantity of water without decomposition; it is de by dissolving mercury in an excess of cold dilute nitric acid.

When excess of mercury has been employed, a finely crystallized basic lt is, after some time, deposited, containing $3Hg_2O,2NO_5+3HO$; this is so decomposed by water. The two salts are easily distinguished when bbed in a mortar with a little chloride of sodium; the neutral compound ves nitrate of soda and calomel; the basic salt, nitrate of soda and a black mpound of calomel with oxide of mercury. A black substance, called *hnemann's soluble mercury*, is produced when ammonia in small quantity dropped into a solution of the nitrate of the suboxide; it contains $3Hg_2O$, O_5+NH_3, or, according to Sir R. Kane, $2HgO,NO_5+NH_3$: the composition this preparation evidently varies according to the temperature and the ncentration of the solutions.

Nitrates of the Protoxide (*Red Oxide*) *of Mercury*. — By dissolving red oxide mercury in excess of nitric acid and evaporating gently, a syrupy liquid obtained, which, enclosed in a bell-jar over lime or sulphuric acid, desits voluminous crystals and crystalline crusts. The crystals and crusts ve the same composition, $2(HgO,NO_5)+HO$. The same substance is desited from the syrupy liquid as a crystalline powder by dropping it into ncentrated nitric acid. The syrupy liquid itself appears to be a definite mpound containing HgO,NO_5+2HO. By saturating hot dilute nitric acid ith the red oxide, a salt is obtained on cooling which crystallizes in needles, rmanent in the air, containing $2HgO,NO_5+HO$. The preceding crystalsed salts are decomposed by water, with production of compounds more and ore basic as the washing is prolonged or the temperature of the water ised. The nitrates of the protoxide of mercury combine with ammonia.

Sulphate of the Suboxide of Mercury, Hg_2O,SO_3, falls as a white crystalline owder when sulphuric acid is added to a solution of the nitrate of the subxide; it is but slightly soluble in water. *Sulphate of the protoxide*, HgO, O_3, is readily prepared by boiling together oil of vitriol and metallic merury until the latter is wholly converted into a heavy white crystalline power, which is the salt in question; the excess of acid is then removed by vaporation, carried to perfect dryness. Equal weights of acid and metal ay be conveniently employed. Water decomposes the sulphate, dissolving t an acid salt and leaving an insoluble, yellow, basic compound, formerly alled *turpeth* or *turbith mineral*, containing, according to Kane's analysis, HgO,SO_3. Long-continued washing with hot water entirely removes the maining acid, and leaving pure protoxide of mercury.

SUBCHLORIDE OF MERCURY; CALOMEL; Hg_2Cl. — This very importont subtance may be easily and well prepared by pouring a solution of the nitrate of he suboxide into a large excess of dilute solution of common salt. It falls s a dense white precipitate, quite insoluble in water; it must be thoroughly ashed with boiling distilled water, and dried. Calomel is generally proared by another and more complex process. Dry sulphate of the red oxide rubbed in a mortar with as much metallic mercury as it already contains, nd a quantity of common salt, until the globules disappear, and an uniform ixture has been produced. This is subjected to sublimation, the vapour of e calomel being carried into an atmosphere of steam, or into a chamber ntaining air; it is thus condensed in a minutely-divided state, and the la-

borious process of pulverization of the sublimed mass avoided. The reaction is thus explained:[1]—

1 eq. sulphate of mercury { 1 eq. mercury, 1 eq. oxygen, 1 eq. sulphuric acid. } — Calomel, $HgCl$.
1 eq. metallic mercury
1 eq. common salt { 1 eq. chlorine, 1 eq. sodium } — Sulphate of soda.

Pure calomel is a heavy, white, insoluble, tasteless powder; it rises in vapour at a temperature below redness, and is obtained by ordinary sublimation as a yellowish-white crystalline mass. It is as insoluble in cold diluted nitric acid as the chloride of silver; boiling-hot strong nitric acid oxidizes and dissolves it. Calomel is instantly decomposed by an alkali, or lime-water, with production of sub-oxide. It is sometimes apt to contain a little chloride, which would be a very dangerous contamination in calomel employed for medical purposes. This is easily discovered by boiling with water, filtering the liquid, and adding caustic potassa. Any corrosive sublimate is indicated by a yellow precipitate.

PROTOCHLORIDE OF MERCURY; CORROSIVE SUBLIMATE; $HgCl$. — The chloride may be obtained by several different processes. (1) When metallic mercury is heated in chlorine gas, it takes fire and burns, producing this substance. (2) It may be made by dissolving the red oxide in hot hydrochloric acid, when crystals of corrosive sublimate separate on cooling. (3) Or, more economically, by subliming a mixture of equal parts of sulphate of the red oxide of mercury and dry common salt; and this is the plan generally followed. The decomposition is thus easily explained:[2]—

1 eq. sulphate of mercury............ { 1 eq. mercury, 1 eq. oxygen, 1 eq. sulphuric acid } — Corrosive sublimate.
1 eq. common salt { 1 eq. chlorine, 1 eq. sodium } — Sulphate of soda.

The sublimed protochloride forms a white, transparent, crystalline mass, of great density; it melts at 509° (265°C), and boils and volatilizes at a somewhat higher temperature. It is soluble in 16 parts of cold and 3 of boiling water, and crystallizes from a hot solution in long white prisms. Alcohol and ether also dissolves it with facility; the latter even withdraws it from a watery solution. Chloride of mercury combines with a great number

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[1] If the grey oxide be considered as protoxide, the sulphate will be sulphate of the binoxide, HgO_2, $2SO_3$, and the decomposition will stand thus:—

1 eq. sulphate of mercury { 1 eq. mercury, 2 eq. oxygen, 2 eq. sulphuric acid } — 2 eq. calomel, $HgCl$.
1 eq. metallic mercury
2 eq. common salt { 2 eq. chlorine, 2 eq. sodium } — 2 eq. sulphate of soda.

Or on the other supposition:—

1 eq. sulphate of mercury .... { 1 eq. mercury, 2 eq. oxygen, 2 eq. sulphuric acid } — Bichloride of mercury.
2 eq. common salt { 2 eq. chlorine, 2 eq. sodium } — 2 eq. sulphate of soda.

other metallic chlorides, forming a series of beautiful double salts, of which the ancient *sal alembroth* may be taken as a good example: it contains $HgCl+NH_4Cl+HO$. Corrosive sublimate absorbs ammoniacal gas with great avidity, generating a compound supposed to contain $2HgCl+NH_3$.

When excess of ammonia is added to a solution of corrosive sublimate, a white insoluble substance is thrown down, long known under the name of *white precipitate*. Sir Robert Kane, who has devoted much attention to the salts of mercury, represents this white precipitate as a double amide and chloride of mercury, or $HgCl+HgNH_2$, 2 equivalents of chloride of mercury and 1 of ammonia, yielding 1 equivalent of the new body and 1 of hydrochloric acid. A corresponding black compound, $Hg_2Cl+HgNH_2$, is produced when ammonia is digested with calomel, which must be carefully distinguished from the suboxide.

Several compounds of protochloride of mercury with protoxide of mercury also exist. These are produced by several processes, as when an alkaline carbonate or bicarbonate is added in varying proportions to a solution of corrosive sublimate. They differ greatly in colour and physical character, and are mostly decomposed by water.

Corrosive sublimate forms insoluble compounds with many of the azotized organic principles, as albumin, &c. It is perhaps to this property that its great antiseptic virtues are due. Animal and vegetable substances are preserved by it from decay, as in Mr. Kyan's method of preserving timber and cordage. Albumin is on this account an excellent antidote to corrosive sublimate in cases of poisoning.

SUBIODIDE OF MERCURY, Hg_2I. — The subiodide is formed when a solution of iodide of potassium is added to nitrate of the suboxide of mercury; it separates as a dirty yellow, insoluble precipitate, with a cast of green. It may be prepared by rubbing together in a mortar mercury and iodine in the proportion of 2 equivalents of the former to 1 of the latter, the mixture being moistened from time to time with a little alcohol.

PROTIODIDE OF MERCURY, HgI. — When solution of iodide of potassium is mixed with protochloride of mercury, a precipitate falls, which is at first yellow, but in a few moments changes to a most brilliant scarlet, which colour is retained on drying. This is the neutral iodide; it may be made, although of rather duller tint, by triturating single equivalents of iodine and mercury with a little alcohol. When prepared by precipitation, it is better to weigh out the proper proportions of the two salts, as the iodide is soluble in an excess of either, more especially in excess of iodide of potassium. The iodide of mercury exhibits a very remarkable case of dimorphism, attended with difference of colour, the latter being red or yellow, according to the figure assumed. Thus, when the iodide is suddenly exposed to a high temperature, it becomes bright yellow throughout, and yields a copious sublimate of minute but brilliant yellow crystals. If in this state it be touched by a hard body, it instantly becomes red, and the same change happens spontaneously after a certain lapse of time. On the other hand, by a very slow and careful heating, a sublimate of red crystals, having a totally different form, may be obtained, which are permanent. The same kind of change happens with the freshly precipitated iodide, as Mr. Warington has shown the yellow crystals first formed breaking up in the course of a few seconds from the passage of the salt to the red modification.[1]

SUBSULPHIDE OF MERCURY, Hg_2S. — The black precipitate thrown down from a solution of the nitrate of suboxide of mercury by sulphuretted hydrogen, is a subsulphide; it is decomposed by heat into metallic mercury and neutral sulphide.

[1] *Memoirs of Chemical Society of London*, i. 85.

SULPHIDE OF MERCURY; ARTIFICIAL CINNABAR; VERMILION; HgS.—Sulphuretted hydrogen gas causes a precipitate of a white colour when passed in small quantity into a solution of corrosive sublimate or nitrate of the red oxide; this is a combination of sulphide with the salt itself. An excess of the gas converts the whole into sulphide, the colour at the same time changing to black. When this black sulphide is sublimed, it becomes dark red and crystalline, but undergoes no change of composition; it is then cinnabar. The sulphide is most easily prepared by subliming an intimate mixture of 6 parts of mercury and 1 of sulphur, and reducing to a very fine powder the resulting cinnabar, the beauty of the tint depending much upon the extent to which division is carried. The red or crystalline sulphide may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of pentasulphide of potassium; the sulphide of mercury is in fact soluble to a certain extent in the alkaline sulphides, and forms with them crystallizable compounds.

When vermilion is heated in the air, it yields metallic mercury and sulphurous acid; it resists the action both of caustic alkali in solution, and of strong mineral acids, even nitric, and is only attacked by *aqua regia*.

When protoxide of mercury is put into a large excess of pure caustic ammonia, a compound is obtained, the colour of which varies with the state of the oxide. If the latter be amorphous, it is pale yellow; if crystallized, then the action of the ammonia is much less energetic, and the product darker in colour. This substance possesses very extraordinary properties, those, namely, of a most powerful base, and probably belongs to the same class as the compound bases containing platinum, described under that metal. The body in question bears a temperature of 260° (126°·6C) without decomposition, becoming brown and anhydrous by the loss of 3 equivalents of water. In this state it contains $NH_2Hg_4O_3 = NH_2Hg_2O + 2HgO$ or $NHg_4O + 2HO$. It is insoluble in water, alcohol, and ammonia; cold solution of potassa has no action on the hydrate, but at a boiling heat some ammonia is disengaged. The anhydrous base is only acted on by hydrate of potassa in fusion. It combines directly and energetically with acids, forming well-defined compounds; it absorbs carbonic acid with avidity from the air, like baryta or lime. It even decomposes ammoniacal salts by boiling, expelling the ammonia and combining with the acid.[1]

The salts of mercury are all volatilized or decomposed by a temperature of ignition; those which fail to yield the metal by simple heating may in all cases be made to do so by heating in a test-tube with a little dry carbonate of soda. The metal is precipitated from its soluble combinations by a plate of copper, and also by a solution of protochloride of tin, used in excess. The behaviour of the protochloride and soluble salts of the red oxide with caustic potassa and ammonia is also highly characteristic.

Alloys of mercury with other metals are termed *amalgams*; mercury dissolves in this manner many of the metals, as gold, silver, tin, lead, &c. These combinations sometimes take place with considerable violence, as in the case of potassium, where light and heat are produced; besides this, many of the amalgams crystallize after a while, becoming solid. The amalgam of

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[1] Ann. Chim. et Phys. 3d series, xviii. 333.

n used in silvering looking-glasses, and that of silver sometimes employed or stopping hollow teeth, are examples.

PLATINUM.

Platinum, palladium, rhodium, iridium, ruthenium, and osmium, form a small group of metals, allied in some cases by properties in common, and still more closely by their natural association. *Crude platinum*, a native alloy of platinum, palladium, rhodium, iridium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials, on the slope of the Ural Mountains in Russia, in Ceylon, and in a few other places. It has never been seen in the rock, which, however, is judged, from the accompanying minerals, to have been serpentine. It is stated to be always present in small quantities with native silver.

From this substance platinum is prepared by the following process:—The crude metal is acted upon as far as possible by nitro-hydrochloric acid, containing an excess of hydrochloric acid, and slightly diluted with water, in order to dissolve as small a quantity of iridium as possible; to the deep yellowish-red and highly acid solution thus produced sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonio-chloride. This substance is washed with a little cold water, dried and heated to redness; metallic platinum in spongy state is left. Although this metal cannot be fused into a compact mass by any furnace-heat, yet the same object may be accomplished by taking advantage of its property of welding, like iron, at a very high temperature. The spongy platinum is made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water is squeezed out, and the mass rendered at length sufficiently solid to bear handling. It is then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure by suitable means. If this operation has been properly conducted, the platinum will now be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire, at pleasure.

Platinum is in point of colour a little whiter than iron; it is exceedingly malleable and ductile, both hot and cold, and is very infusible, melting only before the oxy-hydrogen blowpipe. It is the (except Iridium) heaviest substance known, its specific gravity being 21·5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature; hence its high value in the construction of chemical vessels. It is dissolved by *aqua regia*, and superficially oxidized by fused hydrate of potassa, which enters into combination with the oxide.

The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed. There is a still more curious state in which platinum can be obtained, that of *platinum-black*, where the division is pushed much farther. It is easily prepared by boiling a solution of bichloride of platinum to which an excess of carbonate of soda and a quantity of sugar have been added, until the precipitate formed after a little time becomes perfectly black, and the supernatant liquid colourless. The black powder is collected on a filter, washed, and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent: when placed in contact with a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid; alcohol, dropped on the platinum-black, becomes changed by oxidation to acetic acid, the rise of temperature being often sufficiently great to cause inflammation. When exposed to a red-heat, the black substance shrinks in volume, assumes the appearance of common spongy platinum, and

loses these peculiarities, which are no doubt the result of its excessively comminuted state. Platinum forms two compounds with oxygen, chlorine, &c. The equivalent of platinum is 98·7.[1] Its symbol is Pt.

Protoxide of platinum, PtO. — When protochloride of platinum is digested with caustic potassa, a black powder, soluble in excess of alkali, is produced: this is the protoxide. It is soluble in acids with brown colour and the solutions are not precipitated by sal-ammoniac. When binoxide of platinum is heated with solution of oxalic acid, it is reduced to protoxide, which remains dissolved. The liquid has a dark blue colour, and deposits fine copper-red needles of oxalate of the protoxide of platinum.

Binoxide of platinum, PtO_2. — This is best prepared by adding nitrate of baryta to sulphate of the binoxide of platinum, sulphate of baryta and nitrate of the binoxide are produced. From the latter, caustic soda precipitates one-half of the binoxide of platinum. The sulphate is itself obtained by acting with strong nitric acid upon the bisulphide of platinum, which falls as a black powder when a solution of bichloride is dropped into sulphide of potassium. The hydrate of the binoxide is a bulky brown powder, which, when gently heated, becomes black and anhydrous. It may also be formed by boiling bichloride of platinum with a great excess of caustic soda, and then adding acetic acid. It dissolves in acids, and also combines with bases; the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalis and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. A combination of binoxide of platinum with ammonia exists, which is explosive. Both oxides of platinum are reduced to the metallic state by ignition.

Protochloride of platinum, PtCl.—The protochloride is produced when bichloride of platinum, dried and powdered, is exposed for some time to a heat of 400° (204°·5C), by which half of the chlorine is expelled; also, when sulphurous acid is passed into a solution of the bichloride until the latter ceases to give a precipitate with sal-ammoniac. It is a greenish-grey powder, insoluble in water, but dissolved by hydrochloric acid. The latter solution, mixed with sal-ammoniac or chloride of potassium, deposits a double salt in fine red prismatic crystals, containing in the last case, PtCl + KCl. The corresponding sodium-compound is very soluble and difficult to crystallize. The protochloride is decomposed by heat into chlorine and metallic platinum.

Bichloride or perchloride of Platinum, $PtCl_2$.—This substance is always formed when platinum is dissolved in nitro-hydrochloric acid. The acid solution yields on evaporation to dryness a red or brown residue, deliquescent, and very soluble both in water and alcohol; the aqueous solution has a pure orange-yellow tint. Bichloride of platinum combines to double salts with a great variety of metallic chlorides; the most important of these compounds are those containing the metals of the alkalis and ammonium. *Bichloride of platinum and chloride of potassium*, $PtCl_2$, KCl, forms a bright yellow crystalline precipitate, being produced whenever solutions of the chlorides of platinum and of potassium are mixed, or a salt of potassa, mixed with a little hydrochloric acid, added to bichloride of platinum. It is feebly soluble in water, still less soluble in dilute alcohol, and is decomposed with some difficulty by heat. It is readily reduced by hydrogen at a high temperature, furnishing a mixture of chloride of potassium and platinum-black; the latter substance may thus, indeed, be very easily prepared. The *sodium-salt*, $PtCl_2$, NaCl + 6HO, is very soluble, crystallizing in large, transparent, yellow-red prisms of great beauty. The *ammonio-chloride of platinum*, $PtCl_2$, NH_4Cl, is indistinguishable, in physical characters, from the potassium-salt;

[1] 98·94, Prof. Andrews, Chem. Gaz., Oct. 1852.

is thrown down as a precipitate of small, transparent, yellow, octahedral crystals when sal-ammoniac is mixed with chloride of platinum; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen are driven off. Compounds of platinum with iodine, bromine, sulphur, and phosphorus have been formed, but are comparatively unimportant.

Some very extraordinary compounds have been derived from the protochloride of platinum.

When ammonia in excess is added to a hot solution of the protochloride of platinum and ammonium, a green crystalline salt separates after a time, which is quite insoluble in water, and is not affected by hydrochloric or sulphuric acids, ammonia, or even a boiling-hot solution of potassa. This substance is known as the *green salt of Magnus*, and contains the elements of protochloride of platinum and ammonia, or $PtCl+NH_3$.

When the above compound is heated with concentrated nitric acid, it becomes converted into a white, granular, crystalline powder, which on addition of water dissolves, leaving a residue of metallic platinum. The solution yields on standing small, brilliant, colourless prisms of a substance very soluble in water, containing the elements of protochloride of platinum, ammonia, nitric acid, and an additional equivalent of oxygen:—

$$PtCl,N_2H_6O+NO_5.$$

The platinum and chlorine in this curious body are insensible to ordinary reagents, and ammonia is evolved from it only on boiling with caustic alkali; the presence of nitric acid can be detected immediately by gently heating a small portion with copper-filings and oil of vitriol. From this substance a series of salt-like bodies can be obtained, some of which have been carefully studied by M. Gros. Thus, when treated with hydrochloric acid, the nitric acid is wholly displaced, and a compound formed which crystallizes in small, transparent, yellowish octahedrons, sparingly soluble in boiling water, containing $PtCl,N_2H_6Cl$. With sulphuric acid it gives a substance which crystallizes in small, sparingly soluble, colourless needles, containing $PtCl,N_2H_6O+SO_3$. The oxalic acid compound is white and insoluble; it contains $PtCl,N_2H_6O+C_2O_3$. Crystallizable compounds containing phosphoric, tartaric, citric, malic, formic, and even carbonic acids, were obtained by similar means. These substances have very much the characters of salts of a compound base or *quasi*-metal containing $PtCl,N_2H_6$, and which yet remains unknown in a separate state. M. Raewsky has repeated and extended the observations of M. Gros.

MM. Reiset and Peyrone have also described two other basic bodies containing platinum in the same remarkable condition: these differ from the preceding in being free from chlorine.

Protochloride of platinum put into ammonia becomes rapidly converted into a green powder, which, by boiling, slowly dissolves; the solution, on evaporation and cooling, furnishes beautiful yellowish crystals of the chlorine-compound of one of these bases, compounded of platinum and the elements of ammonia. The crystals contained PtN_2H_6Cl+HO. The equivalent of water is easily expelled by heat, and regained by absorption from the air. The green salt of Magnus, boiled with ammonia, yields the same product.

A solution of this substance, mixed with nitrate of silver, gives chloride of silver and the nitrate of the new base, which crystallizes on evaporation in fine, white, transparent needles, containing $PtN_2H_6O+NO_5$. The sulphide, iodide, and bromide are also crystallizable. Two carbonates exist. By adding baryta-water *to a solution of the* sulphate, or by treating the chloride with *oxide of silver, and evaporating* the filtered liquid in vacuo, a white

crystalline, deliquescent mass is obtained, which is the hydrate of the new base PtN_2H_6O+HO. It is almost comparable in point of alkalinity with potash itself, absorbing carbonic acid with energy, and decomposing ammoniacal salts. When this hydrate is heated to 230° (110°C), it abandons water and ammonia, and leaves a greyish, porous, insoluble mass containing $PtNH_2O$. This is probably an isomeric modification of the second base, whose salts are mentioned below.

When a solution of the iodide, PtN_2H_6I, is long boiled, it deposits a sparingly soluble yellow powder, the composition of which is expressed by the formula $PtNH_3I$: this is the iodine-compound of a second basic substance, $PtNH_3$; and from it by double decomposition a series of analogous salts can be obtained. When the iodine-compound is treated with protoxide of silver, the base itself is obtained in the form of a powerfully alkaline solution. The green salt of Magnus has the same composition as the chloride of this new base, which is yellow and soluble in boiling water, and may be converted into it. The salts of the first base are generally convertible into those of the second by heat, and the converse change may also be often effected by ebullition with ammonia.

The subject of the platinum-bases appears to be by no means exhausted. Only quite recently another remarkable basic compound containing ammonia and platinum has been discovered by M. Gerhardt. The chloride of Reiset's second base, the compound $PtNH_3Cl$, when treated with chlorine, absorbs this element, and becomes converted into a lemon-yellow powder, consisting of small octahedrons, and having the composition $PtNH_3Cl_2$. Boiled with nitrate of silver, this substance yields chloride of silver and, according to the quantity of nitric acid present, a salt, $PtNH_3O_2,2NO_5$, or $PtNH_3O_2,NO_5+2HO$. On adding ammonia to the latter nitrate, a crystalline precipitate takes place, which consists of $PtNH_3O_2+2HO$. This substance, which is slightly soluble in water, may be viewed as the hydrated base existing in the bichloride and in the nitrates previously described.

The bichloride, or a solution of binoxide of platinum, can be at once recognized by the yellow precipitate with sal-ammoniac, decomposable by heat, with production of spongy metal.

Bichloride of platinum and the sodio-chloride of platinum are employed in analytical investigations to detect the presence of potassa, and separate it from soda. For the latter purpose, the alkaline salts are converted into chlorides, and in this condition mixed with four times their weight of sodio-chloride of platinum in crystals, the whole being dissolved in a little water. When the formation of the yellow salt appears complete, alcohol is added, and the precipitate collected on a weighed filter, washed with weak spirit, carefully dried, and weighed. The chloride of potassium is then easily reckoned from the weight of the double salt, and this, subtracted from the weight of the mixed chlorides employed, gives that of the chloride of sodium by difference; 100 parts of potasso-chloride of platinum correspond to 30·56 parts of chloride of potassium.

Capsules and crucibles of platinum are of great value to the chemist; the latter are constantly used in mineral analysis for fusing siliceous matter with alkaline carbonates. They suffer no injury in this operation, although the caustic alkali roughens and corrodes the metal. The experimenter must be particularly careful to avoid introducing any oxide of any easily fusible metal, as that of lead or tin, into a platinum crucible. If reduction should by any means occur, these metals will at once alloy themselves with the pla-

ıd the vessel will be destroyed. A platinum crucible must never be ɜd into the fire, but be always placed within a covered earthen

PALLADIUM.

lution of crude platinum, from which the greater part of that metal precipitated by sal-ammoniac, is neutralized by carbonate of soda, ɜd with a solution of cyanide of mercury; cyanide of palladium as a whitish insoluble substance, which, on being washed, dried, ɜd to redness, yields metallic palladium in a spongy state. The pal- then welded into a mass, in the same manner as platinum.

.um closely corresponds with platinum in colour, appearance, and usibility; it is also very malleable and ductile. In density it differs ꞁh from that metal, being only 11·8. Palladium is more oxidable inum. When heated to redness in the air, especially in the state e, it acquires a blue or purple superficial film of oxide, which is luced at a white heat. This metal is slowly attacked by nitric acid; olvent is *aqua regia*. There are two compounds of palladium and

ꞁuivalent of palladium is 53·3; its symbol is Pd.

XIDE OF PALLADIUM, PdO.—This is obtained by evaporating to dry- l cautiously heating, the solution of palladium in nitric acid. It is .d but little soluble in acids. The hydrate falls as a dark brown te when carbonate of soda is added to the above solution. It is ɜed by a strong heat.

:DE OF PALLADIUM, PdO_2.—The pure binoxide is very difficult to When solution of caustic potassa is poured, little by little, with stirring, upon the double chloride of palladium and potassium in a , the latter is converted into a yellowish-brown substance, which is :ide, in combination with water and a little alkali. It is but feebly ı acids.

:HLORIDE OF PALLADIUM, PdCl.—The solution of the metal in *aqua* ds this substance when evaporated to drynesss. It is a dark brown luble in water when the heat has not been too great, and forms alts with many metallic chlorides. The potassio- and ammonio- of palladium are much more soluble than those of platinum; they :ownish-yellow tint.

)RIDE OF PALLADIUM only exists in solution, and in combination with ine chlorides. It is formed when the protochloride of palladium is in *aqua regia*. The solution has an intense brown colour, and is ɜed by evaporation. Mixed with chloride of potassium or sal-ammo- ives rise to a red crystalline precipitate of double salt which is but ıble in water.

ıide of palladium, PdS, is formed by fusing the metal with sulphur, ıcipitating a solution of protochloride by sulphuretted hydrogen.

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adium-salt is well marked by the pale yellowish-white precipitate ıtion of cyanide of mercury, convertible by heat into the spongy This precipitate is a double salt, having the formula PdCy,HgCy,HO.

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ium is readily alloyed with other metals, as copper: one of these ds, namely, the alloy with silver, has been applied to useful pur- A native alloy of gold with palladium is found in the Brazils, and *into England.*

RHODIUM.

The solution from which platinum and palladium have been separated in the manner described is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol of specific gravity 0·837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water; chloride of sodium is dissolved out, and metallic rhodium remains. Thus obtained, rhodium is a white, coherent, spongy mass, which is more infusible and less capable of being welded than platinum. Its specific gravity varies from 10·6 to 11.

Rhodium is very brittle: reduced to powder and heated in the air, it becomes oxidized, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potassa. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which it is attacked by *aqua regia*.

The equivalent of rhodium is 52·2; its symbol is R.

Protoxide of rhodium, RO, is obtained by roasting finely divided metallic rhodium. It is but little known.

Sesquioxide of rhodium, R_2O_3. — Finely-powdered metallic rhodium is heated in a silver crucible with a mixture of hydrate of potassa and nitre; the fused mass boiled with water leaves a dark brown, insoluble substance, consisting of sesquioxide of rhodium in union with potassa. This is digested with hydrochloric acid, which removes the potassa and leaves a greenish-grey hydrate of the sesquioxide of rhodium, insoluble in acids. A soluble modification of the same substance, retaining, however, a portion of alkali, may be had by adding an excess of carbonate of potassa to the double chloride of rhodium and potassium, and evaporating.

Sesquichloride of rhodium, R_2Cl_3. — The pure sesquichloride is prepared by adding hydrofluosilicic acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red colour. It is decomposed by heat into chlorine and metallic rhodium. The *chloride of rhodium and potassium*, $R_2Cl_3+2KCl+2HO$, is prepared by heating in a stream of chlorine a mixture of equal parts finely powdered rhodium and chloride of potassium. This salt has a fine red colour, is soluble in water, and crystallizes in four-sided prisms. *Chloride of rhodium and sodium* is also a very beautiful red salt, obtained by a similar process: it contains $R_2Cl_3+3NaCl+18HO$. The *chloride of rhodium and ammonium* resembles the potassium-compound.

Sulphate of rhodium, $R_2O_3.3SO_3$. — The sulphide of rhodium, obtained by precipitating one of the salts by a soluble sulphide, is oxidized by strong nitric acid. The product is a brown powder, nearly insoluble in nitric acid, but dissolved by water; it cannot be made to crystallize. *Sulphate of rhodium and potassium*, is produced when metallic rhodium is strongly heated with bisulphate of potassa. It is a yellow salt, slowly soluble in cold water.

An alloy of steel with a small quantity of rhodium is said to possess extremely valuable properties.

IRIDIUM.

When crude platinum is dissolved in *aqua regia*, a small quantity of a grey scaly metallic substance usually remains behind, having altogether resisted the action of the acid; this is a native alloy of *iridium* and *osmium*. It is reduced to powder, mixed with an equal weight of dry chloride of sodium, and heated to redness in a glass tube, through which a stream of moist chlo-

ne gas is transmitted. The farther extremity of the tube is connected with receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, chloride of iridium and chloride of osmium being produced: the former remains in combination with the chloride of sodium; the latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the double chloride of iridium and sodium is dissolved out: this is mixed with an excess of carbonate of soda, and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of sesquioxide of iron, and combination of oxide of iridium with soda; it is reduced by hydrogen at high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.

Iridium is a white brittle metal, fusible with great difficulty before the oxy-hydrogen blowpipe.[1] It is not attacked by any acid, but is oxidized by fusion with nitre, and by ignition to redness in the air.

The equivalent of iridium is 99. Its symbol is Ir.

OXIDES OF IRIDIUM.—Four of these compounds are described. *Protoxide of iridium*, IrO, is prepared by adding caustic alkali to the protochloride, and digesting the precipitate in an acid. It is a heavy black powder, insoluble in acids. It may be had in the state of hydrate by precipitating the protochloride of iridium and sodium by caustic potassa. The hydrate is soluble in acids with dirty green colour. *Sesquioxide*, Ir_2O_3, is produced when iridium is heated in the air, or with nitre; it is best prepared by fusing in a silver crucible a mixture of carbonate of potassa and the terchloride of iridium and potassium, and boiling the product with water. This oxide is bluish-black, and is quite insoluble in acids. It is reduced by combustible substances with explosion. *Binoxide of iridium*, IrO_2, is unknown in a separate state; it is supposed to exist in the sulphate, produced when the sulphide is oxidized by nitric acid. A solution of sulphate heated with excess of alkali evolves oxygen gas, and deposits sesquioxide of iridium. *Teroxide of iridium*, IrO_3, is produced when carbonate of potassa is gently heated with the terchloride of iridium; it forms a greyish-yellow hydrate, which contains alkali.

CHLORIDES OF IRIDIUM. —*Protochloride*, IrCl, is formed when the metal is brought in contact with chlorine at a dull red-heat; it is a dark olive-green insoluble powder. It is dissolved by hydrochloric acid, and forms double salts with the alkaline chlorides, which have a green colour. The *sesquichloride*, Ir_2Cl_3, is prepared by strongly heating iridium with nitre, adding water, and enough nitric acid to saturate the alkali, warming the mixture, and then dissolving the precipitated hydrate of the sesquioxide in hydrochloric acid. It forms a dark yellowish-brown solution. This substance combines with metallic chlorides. *Bichloride of iridium* is obtained in solution by adding hydrofluosilicic acid to the bichloride of iridium and potassium, formed when chlorine is passed over a heated mixture of iridium and chloride of potassium. It forms with metallic chlorides a number of double salts, which resemble the platinum-compounds of the same order. *Terchloride of iridium*, $IrCl_3$, is unknown in a separate state. *Terchloride of iridium and potassium* is obtained by heating iridium with nitre, and then dissolving the

[1] It is the heaviest substance known, its specific gravity, according to Professor Hare, being 21.8. *Proceedings of the Amer. Phil. Soc.* May and June, 1842. — R. B

whole in *aqua regia*, and evaporating to dryness. The excess of chloride of potassium may be extracted by a small quantity of water. The crystallized salt has a beautiful red colour. The variety of tints exhibited by the different soluble compounds of iridium is very remarkable, and suggested the name of the metal, from the word *iris*.

Platinum, palladium, and iridium combine with carbon when heated in the flame of a spirit-lamp; they acquire a covering of soot, which, when burned, leaves a kind of skeleton of spongy metal.

RUTHENIUM.

M. Claus has described under this name a new metal contained in the residue from crude platinum, insoluble in *aqua regia*. It closely resembles iridium in its general characters, but yet possesses distinctive features of its own. It was obtained in the form of small angular masses, with perfect metallic lustre, very brittle and infusible. Its specific gravity is 8·6. It resists the action of acids, but oxidizes readily when heated in the air.

The equivalent of ruthenium is 52·2, and its symbol Ru.

OXIDES OF RUTHENIUM. — *Protoxide of ruthenium*, RuO, is a greyish-black metallic-looking powder, obtained by heating bichloride of ruthenium with excess of carbonate of soda in a stream of carbonic acid gas, and then washing away the soluble saline matter. It is insoluble in acids. The *sesquioxide*, Ru_2O_3, in the anhydrous condition is a bluish-black powder formed by heating the metal in the air. It is also precipitated by alkalis from the sesquichloride as a blackish-brown hydrate, soluble in acids with orange-yellow colour. The *binoxide*, RuO_2, is a deep blue powder, procured by roasting the bisulphide. A hydrate of this oxide is known in an impure condition. An *acid* of ruthenium is also supposed to exist.

Sesquichloride of ruthenium, Ru_2Cl_3, is an orange-yellow soluble salt of astringent taste; when the solution is heated, it becomes green and finally blue, by reduction, in all probability, to protochloride. Sesquichloride of ruthenium forms double salts with the chlorides of potassium and ammonium.

OSMIUM.

The solution of osmic acid in ammonia, already mentioned, is gently heated for some time in a loosely-stopped vessel; its original yellow colour becomes darker, and at length a brown precipitate falls, which is a combination of sesquioxide of osmium with ammonia: it results from the reduction of the osmic acid by the hydrogen of the volatile alkali. A little of the precipitate is held in solution by the sal-ammoniac, but may be recovered by heating the clear liquid with caustic potassa. The brown substance is dissolved in hydrochloric acid, a little chloride of ammonium added, and the whole evaporated to dryness. The residue is strongly heated in a small porcelain retort; the oxygen of the oxide combines with hydrogen from the ammonia, vapour of water, hydrochloric acid, and sal-ammoniac are expelled, and osmium left behind, as a greyish porous mass, having the metallic lustre.

In the most compact state in which this metal can be obtained, it has a bluish-white colour, and, although somewhat flexible in thin plates, is yet easily reduced to powder. Its specific gravity is 10: it is neither fusible nor volatile. It burns when heated to redness, yielding osmic acid, which volatilizes. Osmate of potassa is produced when the metal is fused with nitre. When in a finely divided state, it is oxidized by strong nitric acid.

The equivalent of osmium is 99·6; its symbol is Os.

OXIDES OF OSMIUM.—Five compounds of osmium with oxygen are known. *Protoxide*, OsO, is obtained, in combination with a little alkali, when caustic potassa is added to a solution of protochloride of osmium and potassium. It is a dark green powder, slowly soluble in acids. Sesquioxide, Os_2O_3, has

een noticed; it is generated by the deoxidation of osmate of am-
t is black, and but little soluble in acids. It always contains and explodes feebly when heated. *Binoxide of osmium*, OsO_2, is pre- strongly heating in a retort a mixture of carbonate of soda and the of osmium and potassium, and treating the residue with water, and s with hydrochloric acid. The binoxide is a black powder, insoluble and burning to osmic acid when heated in the air. *Osmious acid* nown only in combination. On adding alcohol to a solution of potassa, the alcohol is oxidized at the expense of the osmic acid, e-red crystalline powder of osmite of potassa is produced. On at- to separate the acid, it is decomposed into the binoxide and osmic *mic acid*, OsO_4, is by far the most important and interesting of the this metal. It is prepared by heating osmium in a current of pure is; it condenses in the cool part of the tube in which the experi- ade in colourless transparent crystals. Osmic acid melts and even w 212° (100°C); its vapour has a peculiar offensive odour, and is ly irritating and dangerous. Water slowly dissolves this substance. d properties, and combines with bases. Nearly all the metals pre- smium from a solution of osmic acid. By the action of ammonia acid, a new acid has been formed, containing osmium, nitrogen, en. It has been called osman-osmic acid or osmamic acid. Some e hanging over the formula of this substance. It produces salts y bases.

DES OF OSMIUM.—*Protochloride*, OsCl, is a dark green crystalline , formed by gently heating osmium in chlorine gas. It is soluble quantity of water, with green colour, but decomposed by a large nto osmic and hydrochloric acids and metallic osmium. It forms ts with the metallic chlorides. The *sesquichloride*, Os_2Cl_3, has not ted; it exists in the solution obtained by dissolving the sesquioxide hloric acid. *Bichloride*, $OsCl_2$, in combination with chloride of , is produced when a mixture of equal parts metallic osmium and amed salt is strongly heated in chlorine gas. It forms fine red oc- rystals, containing $OsCl_2 + KCl$.

ı combines also with sulphur and with phosphorus.

PART III.

ORGANIC CHEMISTRY.

INTRODUCTION.

ORGANIC substances, whether directly derived from the vegetable or animal kingdom, or produced by the subsequent modification of bodies which thus originate, are remarkable as a class for a degree of complexity of constitution far exceeding that observed in any of the compounds yet described. And yet the number of elements which enter into the composition of these substances is extremely limited; very few, comparatively speaking, contain more than four, viz., carbon, hydrogen, oxygen, and nitrogen; sulphur and phosphorus are occasionally associated with these in certain mineral products; and compounds containing chlorine, bromine, iodine, arsenic, antimony, zinc, &c., have been formed by artificial means. This paucity of elementary bodies is compensated by the very peculiar and extraordinary properties of the four first-mentioned, which possess capabilities of combination to which the remaining elements are strangers. There appears to be absolutely no limit to the number of definite, and often crystallizable, substances which can be thus generated, each marked by a perfect individuality of its own.

The mode of association of the elements of organic substances is in general altogether different from that so obvious in the other division of the science. The latter is invariably characterized by what may be termed a *binary* plan of combination, union taking place between *pairs* of elements, and the compounds so produced again uniting themselves to other compound bodies in the same manner. Thus, copper and oxygen combine to oxide of copper, potassium and oxygen to potassa, sulphur and oxygen to sulphuric acid; sulphuric acid, in its turn, combines both with oxide of copper and oxide of potassium, generating a pair of salts, which are again capable of uniting to form the double compound, CuO,SO_3+KO,SO_3.

The most complicated products of inorganic chemistry may be thus shown to be built up by this repeated pairing on the part of their constituents. With organic bodies, however, the case is strikingly different; no such arrangement can here be traced. In sugar, $C_{12}H_{11}O_{11}$, or morphine, $C_{34}H_{19}NO_6$, or the radical of bitter almond oil, $C_{14}H_5O_2$, and a multitude of similar cases, the elements concerned are, as it were, bound up together into a single whole, which can enter into combination with other substances, and be thence disengaged with properties unaltered.

A curious consequence of this peculiarity is to be found in the comparatively *instable* character of organic compounds, and their general proneness to decomposition and change, when the balance of opposing forces, to which they owe their existence, becomes deranged by some external cause.

If a complex inorganic substance be attentively considered, it will usually be found that the elements are combined in such a manner as to satisfy the most powerful affinities, and to give rise to a state of very considerable permanence and durability. But in the case of an organic substance containing

three or four elements associated in the way described, this is very far from being true: the carbon and oxygen strongly tend to unite to form carbonic acid; the hydrogen and oxygen attract each other in a powerful manner, and the nitrogen, if that body be present, also contributes its share to these internal sources of weakness by its disposition to generate ammonia. While the opposing forces remain exactly balanced, the integrity of the compound is preserved; but the moment one of them, from some accidental cause, acquires preponderance over the rest, equilibrium is destroyed and the organic principle breaks up into two or more new bodies of simpler and more permanent constitution. The agency of heat produces this effect by exalting the attraction of oxygen for hydrogen and carbon; hence the almost universal destructibility of organic substances by a high temperature. Mere molecular disturbance of any kind may cause destruction when the instability is very great.

As a general rule, it may be assumed that those bodies which are most complex from the number of elements, and the want of simplicity in their equivalent relations, are by constitution weakest, and least capable of resisting the action of disturbing forces; and that this susceptibility of change diminishes with increased simplicity of structure, until it reaches its minimum in those bodies which, like the carbides of hydrogen, like cyanogen, and oxalic acid, connect, by imperceptible gradations, the organic and the mineral departments of chemical science.

The definite organic principles of the vegetable and animal kingdoms form but a very small proportion of the immense mass of compounds included within the domain of organic chemistry: by far the greater number of these are produced by modifying by suitable means the bodies furnished by the plant or the animal, and which have themselves been formed from the elements of the air by processes for the most part unknown, carried on under the control of vitality. Unlike these latter, the artificial modifications referred to, by oxidation, by the action of other powerful reagents, by the influence of heat, and by numerous other sources of disturbance, are, for the most part, changes of descent in order of complexity, new products being thus generated more simple in constitution and more stable in character than the bodies from which they were derived. These, in turn, by repetition of such treatment under perhaps varied circumstances, may be broken up into other and still simpler organic combinations; until at length the binary compounds of inorganic chemistry, or bodies so allied to them that they may be placed indifferently in either group, are by such means reached.

Organic Substitution-products: Law of Substitution.—The study of the action of chlorine, bromine, iodine, and nitric acid upon various organic substances has led to the discovery of a very remarkable law regulating the formation of chlorinetted and other analogous compounds, which, without being of necessity absolute in every case, is yet of sufficient generality and importance to require careful consideration. This peculiar mode of action consists in the replacement of the hydrogen of the organic substance by chlorine, bromine, iodine, the elements of hyponitric acid, and more rarely other substances of the same class, equivalent for equivalent, without the destruction of the primitive type or constitution of the compound so modified. The hydrogen thus removed takes of course the form of hydrochloric or hydrobromic acid, &c., or that of water, by combination with another portion of the active body. Strange as it may appear, and utterly opposed to the ordinary views of the functions of powerful salt-radicals, this loss of hydrogen and assumption of the new element do actually occur with a great variety of substances belonging to different groups with comparatively trifling disturbance *of physical and chemical* properties; the power of saturation, the density *of the vapour, and other* pecularities of the original substance remain

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PART I

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ORGANIC C...

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'" ascribed to difference of constitution, the ele- d. For instance, formic ether and acetate of " $C_6H_6O_4$; but then the first is supposed abined with ether, C_4H_5O; while the h the same views, to be made up of ace- wood-spirit, C_2H_3O. And this method of nt and satisfactory; when it can be shown on, or even a difference in the equivalent num- . more bodies identical in ultimate composition, ant characters becomes to a certain extent intelli-

y be thus classified:—

ry *Substances*, and their compounds.—These affect the characters of the true elements, and, like the latter, evince a ite on the one hand with hydrogen and the metals, and on the hlorine, iodine, and oxygen. The former are designated *organic s*, and the latter *organic salt-basyles*. Few of either kind have been d, and it is very possible that very many of them are unable to separate state. Some of these quasi-elements are among the most and interesting substances in organic chemistry.

ic Salt-bases, not being the oxides of known radicals.—The prin- bers of this class are the vegeto-alkalis; they form crystallizable with acids, organic and inorganic, and even possess in some cases lkaline reaction to test-paper.

ic acids, not being compounds of known radicals.—These bodies numerous and important. Many of them have an intensely sour en vegetable blues, and are almost comparable in chemical energy ids of mineral origin.

al non-azotized substances, containing oxygen and hydrogen in the s to form water.—The term *neutral*, as applied to these compounds, tly correct, as they usually manifest feeble acid properties by com- metallic oxides. This group comprehends the sugars, the dif- ifications of starch, gum, &c.

al azotized substances; the albuminous principles and their allies, omponents of the animal frame.—These are in the highest degree constitution, and are destitute of the faculty of crystallization.

les of Hydrogen, their oxides and derivatives.

bodies.

ound acids, containing the elements of an organic substance in com- ith those of a mineral or other acid.—These bodies form a large nteresting class, of which sulphovinic acid may be taken as the presentative.

ring principles, and other substances not referable to either of the classes.

on of heat on organic substances presents many important and points, of which a few of the more prominent may be noticed. imple constitution and of some permanence, which do not sublime . as many of the organic acids, yield, when exposed to a high, but temperature, in a retort, new compounds, perfectly definite and allizable, which partake, to a certain extent, of the properties of l substance: the numerous *pyro-acids*, of which many examples in the succeeding pages, are thus produced. Carbonic acid and often eliminated under these circumstances. If the heat be sud- d to redness, then the regularity of the decomposition vanishes, *roducts become more* uncertain and more numerous; carbonic *tery vapor are* succeeded by inflammable gases as carbonic oxide

and carbonetted hydrogen; oily matter and tar distil over, and increase in quantity until the close of the operation, when the retort is found to contain, in most cases, a residue of charcoal. Such is destructive distillation

If the organic substance contain nitrogen, and be not of a kind capable of taking a new and permanent form at a moderate degree of heat, then that nitrogen is in most instances partly disengaged in the shape of ammonia, or substances analogous to it, partly left in combination with the carbonaceous matter in the distillatory vessel. The products of dry distillation thus become still more complicated.

A much greater degree of regularity is observed in the effects of heat on fixed organic matters, when these are previously mixed with an excess of strong alkaline base, as potassa or lime. In such cases an acid, the nature of which is chiefly dependent upon the temperature applied, is produced, and remains in union with the base, the residual element or elements escaping in some volatile form. Thus, benzoic acid distilled with hydrate of lime, at a dull red-heat, yields carbonate of lime and a bicarbide of hydrogen, benzole; woody fibre and caustic potassa, heated to a very moderate temperature, yield ulmic acid and free hydrogen; with a higher degree of heat oxalic acid appears in the place of the ulmic; and, at the temperature of ignition, carbonic acid, hydrogen being the other product.

The spontaneous changes denominated *decay* and *putrefaction*, to which many more of the complicated organic, and, more particularly, azotized principles are subject, have lately attracted much attention. By the expression *decay*,[1] Liebig and his school understand a decomposition of moist organic matter, freely exposed to the air, by the oxygen of which it is gradually burned and destroyed, without sensible elevation of temperature; the term *putrefaction*, on the other hand, is limited to changes occurring in and beneath the surface of water, the effect being a mere transposition of elements, or metamorphosis of the organic body. The conversion of sugar into alcohol and carbonic acid furnishes, perhaps, the simplest case of the kind. It is proper to remark, however, that contact of oxygen is indispensable, in the first instance, to the change, which, when once begun, proceeds, without the aid of any other substance external to the decomposing body, unless it be water or its elements. Every case of putrefaction thus begins with decay; and if the decay or its cause, namely, the absorption of oxygen, be prevented, no putrefaction occurs. The most putrescible substances, as animal flesh intended for food, milk, and highly azotized vegetables, are preserved indefinitely, by enclosure in metallic cases, from which the air has been *completely* removed and excluded.

Some of the curious phenomena of communicated chemical activity, where a decomposing substance seems to involve others in destructive change, which, without such influence, would have remained in a permanent and quiescent state, will be found noticed in their proper places, as under the head of Vinous Fermentation. These actions are yet very obscure, and require to be discussed with great caution.

THE ULTIMATE ANALYSIS OF ORGANIC BODIES.

As organic substances cannot be produced at will from their elements, the *analytical* method of research is alone applicable to the investigation of their exact chemical composition; hence the ultimate analysis of these substances becomes a matter of great practical importance. The operation is always executed by causing complete combustion of a known weight of the body to

[1] Or eremacausis, that is, slow burning.

ımined, in such a manner that the carbonic acid and water produced ›e collected, and their quantity determined; the carbon and hydrogen espectively contain may from these data be easily calculated. When en, sulphur, phosphorus, chlorine, &c., are present, special and sepaıeans are resorted to for their estimation.

method to be described for the determination of the carbon and hyı owes its convenience and efficiency to the improvements of Professor ;; it has superseded all other processes, and is now invariably employed uiries of the kind. With proper care, the results obtained are wondercorrect; and equal, if not surpass in precision, those of the best al analyses. The principle upon which the whole depends is the fol;:—When an organic substance is heated with the oxides of copper, ınd several other metals, it undergoes complete combustion at the exof the oxygen of the oxide, the metal being at the same time reduced, completely or to a lower state of oxidation. This effect takes place greatest ease and certainty with the black oxide of copper, which, alh unchanged by heat alone, gives up oxygen to combustible matter extreme facility. When nothing but carbon and hydrogen, or those bo›gether with oxygen, are present, one experiment suffices; the carbon ydrogen are determined directly, and the oxygen by difference.

s of course indispensable that the substance to be analyzed should ıs the physical characters of purity, otherwise the inquiry cannot lead good result; if in the solid state, it must also be freed with the most ılous care from the moisture which many substances retain with great acy. If it will bear the application of moderate heat, this desiccation y easily accomplished by a water or steam-bath; in other cases, expo.t common temperatures to the absorbent powers of a large surface of vitriol in the vacuum of an air-pump must be substituted.

operation of weighing the dried powder is conducted in a narrow open fig. 153), about 2½ or 3 inches long; the tube ubstance are weighed together, and, when the has been removed, the tube with any little ent matter is re-weighed. This weight, subd from the former, gives the weight of the sub employed in the experiment. As only 5 or 6 are used, the weighings should not evolve a r error than $\frac{1}{100}$th part of a grain.

Fig. 153.

protoxide of copper is best made from the by complete ignition in an earthen crucible: educed to powder, and re-heated just before expel hygroscopic moisture, which it absorbs, hile warm, with avidity. The combustion is med in a tube of hard white Bohemian glass, a diameter of 0·4 or 0·5 inch, and in length varying from 14 to 18 ; this kind of glass bears a moderate red-heat without becoming soft ı to lose its shape. One end of the tube is drawn out to a point, as in fig. 154, and closed; the other is simply heated to fuse and soften ırp edges of the glass. The tube is now two-thirds filled with the ye

Fig. 154.

warm protoxide of copper, nearly the whole of which is transferred to a small porcelain or Wedgwood mortar, and very intimately mixed with the organic substance. The mixture is next transferred to the tube, and the mortar rinsed with a little fresh and hot oxide, which is added to the rest; the tube is, lastly, filled to within an inch of the open end with oxide from the crucible. A few gentle taps on the table suffice to shake together the contents, so as to leave a free passage for the evolved gases from end to end. The arrangement of the mixture and oxide in the tube is represented in the sketch.

The tube is then ready to be placed in the furnace or chauffer: this latter is constructed of thin sheet-iron, and is furnished with a series of supports of equal height, which serve to prevent flexure in the combustion-tube when softened by heat. Fig. 155. The chauffer is placed upon flat bricks or a

Fig. 155.

piece of stone, so that but little air can enter the grating, unless the wi be purposely raised. A slight inclination is also given towards the extrem occupied by the mouth of the combustion-tube, which passes through a h provided for the purpose.

To collect the water produced in the experiment, a small light tube of the form represented in fig. 156, filled with fragments of spongy chloride of c cium, is attached by a perforated cork, thoroughly dried, to the open e

Fig. 156.

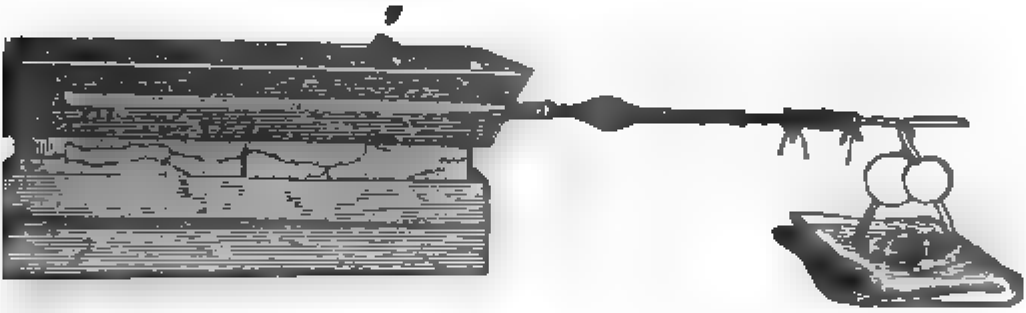
Fig. 157.

tremity of the combustion-tube. The carbonic acid is condensed into a solution of caustic potassa, of specific gravity 1·27, which is contained in a sm glass apparatus on the principle of a Woulfe's bottle, shown in fig. 157. The connection between the latter and the chloride of calcium-tube is com pleted by a little tube of caoutchouc, secured with silk cord. The whole is shown in fig. 158, as arranged for use. Both the chloride of calcium-tube and the potass-apparatus are weighed with the utmost care before the ex periment.

The tightness of the junctions may be ascertained by slightly rarefying the included air by sucking a few bubbles from the interior through the liquid, using the dry lips, or better, a little bent tube with a perforated cork: if the difference of the level of the liquid in the two limbs of the potass

ratus be preserved for several minutes, the joints are perfect. Red-charcoal is now placed around the anterior portion of the combustion-

Fig. 156.



Drawing of the whole arrangement.

e, containing the pure oxide of copper, and when this is red-hot, the fire lowly extended towards the farther extremity by shifting the moveable een *g*, represented in the drawing. The experiment must be so conducted, t an uniform stream of carbonic acid shall enter the potass-apparatus by bles which may be easily counted: when no nitrogen is present, these bles are towards the termination of the experiment almost completely orbed by the alkaline liquid, the little residue of air alone escaping. In case of an azotized body, on the contrary, bubbles of nitrogen gas, pass ugh the potassa-solution during the whole process.

When the tube has become completely heated from end to end, and no e gas is disengaged, but, on the other hand, absorption begins to be ent, the coals are removed from the farther extremity of the combustion-e, and the point of the latter broken off. A little air is drawn through whole apparatus, by which the remaining carbonic acid and watery our are secured. The parts are, lastly, detached, and the chloride of ium tube and potass-apparatus re-weighed. The following account of a experiment will serve as an illustration; the substance examined was tallized sugar.

Quantity of sugar employed	4·750 grains.
Potass-apparatus weighed after experiment....	781·13
" " before experiment..	773·82
Carbonic acid	7·31
Chloride of calcium-tube after experiment......	226·05
" " before experiment ...	223·30
Water	2·75

·31 gr. carbonic acid=1 994 gr. carbon: and 2·75 gr. water=0·3056 gr rogen; or in 100 parts of sugar,[1]

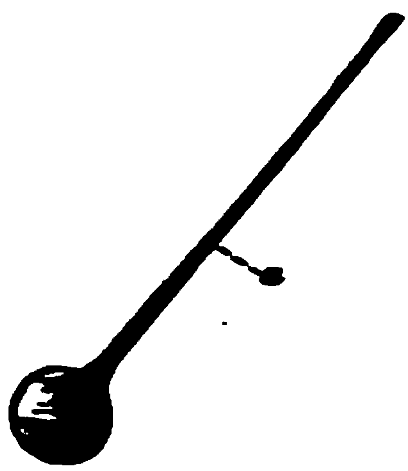
[1] The theoretical composition of sugar $C_{12}H_{11}O_{11}$, reckoned to 100 parts gives—

Carbon........................	42·11
Hydrogen........................	6·43
Oxygen........................	51·46
	100·00

Carbon	41·98
Hydrogen	6·43
Oxygen, by difference	51·59
	100·00

When the organic substances cannot be mixed with the protoxide of co in the manner described, the process must be slightly modified to suit particular case. If, for example, a volatile liquid is to be examined, enclosed in a little glass bulb with a narrow stem, which is weighed be and after the introduction of the liquid, the point being hermetically sea The combustion-tube must have, in this case, a much greater length; as the protoxide of copper cannot be introduced hot, it must be ignited cooled out of contact with the atmosphere, to vent absorption of watery vapour. This is conveniently effected by transferring it, in a ho state, to a large platinum crucible, to whi close-fitting cover can be adapted. When cold, the cover is removed, and instantly repl by a dry glass funnel, by the assistance of w the oxide may be directly poured into the bustion-tube, with mere momentary exposu the air. A little oxide is put in, then the with its stem broken at *a*, fig. 159, a file-scr having been previously made; and lastly, the is filled with the cold and dry protoxide of co It is arranged in the chauffer, the chlorid calcium tube and potass-apparatus adjusted, then, some six or eight inches of oxide having been heated to redness, liquid in the bulb is, by the approximation of a hot coal, expelled, and sl converted into vapour, which, in passing over the hot oxide, is comple burned. The experiment is then terminated in the usual manner. Fu fatty substances, and volatile concrete bodies, as camphor, require ra different management, which need not be here described.

Fig. 159.



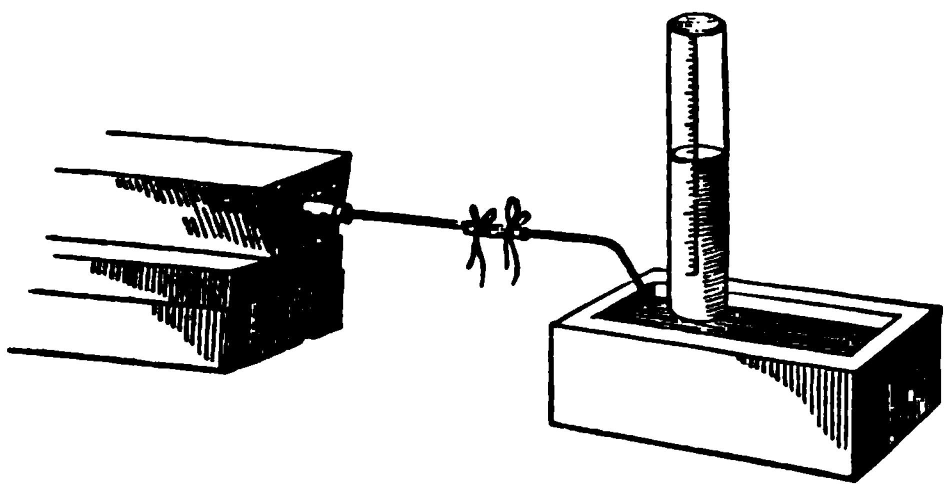
Protoxide of copper, which has been used, may be easily restored moistening with nitric acid, and ignition to redness; it becomes, in rather improved than otherwise, as after frequent employment its densit increased, and its troublesome hygroscopic powers diminished. For stances which are very difficult of combustion, from the large proportion carbon they contain, and for compounds into which chlorine enters as a stituent, fused and powdered chromate of lead is very advantageously stituted for the protoxide of copper. Chromate of lead freely gives oxygen to combustible matters, and even evolves, when strongly heate little of that gas, which thus ensures the perfect combustion of the org body.

Analysis of azotized Substances.—The presence of nitrogen in an org compound is easily ascertained by heating a small portion with solid hyd of potassa in a test-tube: the nitrogen, if present, is converted into am nia, which may be recognized by its odour and alkaline reaction. There several methods of determining the proportion of nitrogen in azotized org substances, the experimenter being guided in his choice of means by nature of the substance and its comparative richness in that element. carbon and hydrogen are first determined in the usual manner, a longer than usual is employed, and four or five inches of its anterior portion f with spongy metallic copper, made by reducing the protoxide by hydro this sor... ny nitrous acid or binoxide of nitrogen, which

ed in the act of combustion. During the experiment some idea of ıdance or paucity of the nitrogen may be formed from the number les of incondensible gas which traverse the solution of potassa.

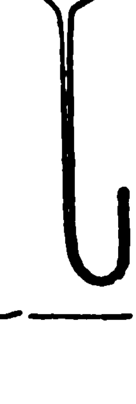
: case of compounds abounding in nitrogen, and readily burned by le of copper, a method may be employed, which is very easy of execu- ıis consists in determining the ratio borne by the liberated nitrogen arbonic acid produced in the combustion. A tube of hard glass, of al diameter, and about 15 inches long, is sealed at one end; a little rganic substance, mixed with protoxide of copper, is introduced, and to occupy about two inches of the tube; about as much pure oxide l over it, and then another portion of a similar mixture; after which ı is filled up with a second and larger portion of the pure oxide, and ity of spongy metallic copper. A short bent tube, made moveable ıutchouc joint, is fitted by a perforated cork, and made to dip into a al trough, while the combustion-tube itself rests in the chauffer. 0.)

Fig. 160.



s first applied to the anterior part of the tube containing the metal nixed oxide, and, when this is red-hot, to the extreme end. Com- of the first portion of the mixture takes place, the gaseous products g before them nearly the whole of the air of the apparatus. o more gas issues, the tube is slowly heated by half an inch ıe, in the usual manner, and all the gas very carefully col- n a graduated jar, until the operation is at an end. The is then read off, and some strong solution of caustic po- rown up into the jar by a *pipette* with a curved extremity. 31.) When the absorption is complete, the residual volume ıgen is observed, and compared with that of the mixed roper correction being made for difference of level in the y, and from these data the exact proportion borne by the ı to the carbon can be at once determined[1]

Fig. 161.



ı proportion of nitrogen be but small, the error from the ni- of the residual atmospheric air becomes so great as to de- l confidence in the result of the experiment; and the same appens when the substance is incompletely burned by pro- of copper; other means must then be employed. The

ᵉᵉ of the two gases represents *equivalents*; for

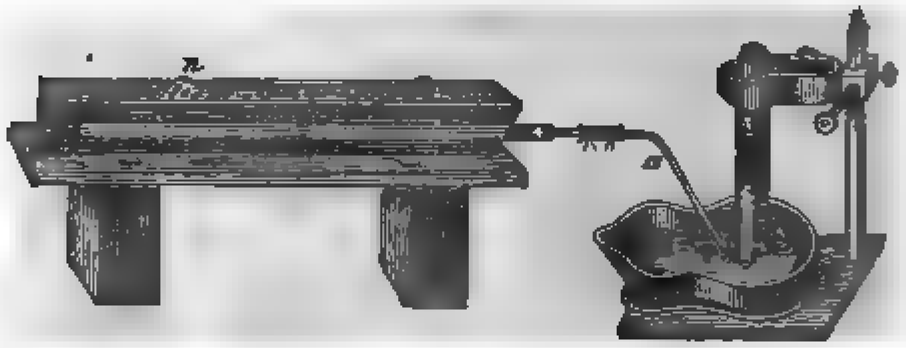
100 cubic inches carbonic acid weigh 47·26 grains.
100 „ nitrogen „ 30·14
47·26 : 30·14 = 22 : 14·01

two terms are *the equivalent* numbers: one equivalent of carbonic acid contains *valent of carbon.*

absolute method of determination, also known by the name of Dumas's method, may be had recourse to when the foregoing, or *comparative* method fails from the first cause mentioned; it gives excellent results, and is applicable to all azotized substances.

A tube of good Bohemian glass, 28 inches long, is securely sealed at one end; into this enough dry bicarbonate of soda is put to occupy 6 inches; a little pure protoxide of copper is next introduced, and afterwards the mixture of oxide and organic substance, the weight of the latter, between 4 and 9 grains, in a dry state, having been correctly determined. The remainder of the tube, amounting to nearly one-half of its length, is then filled with pure protoxide of copper and spongy metal, and a round cork, perforated by a piece of narrow tube, is securely adapted to its mouth. The tube is connected by means of a caoutchouc joint with a bent delivery tube *a*, fig. 162, and the combustion-tube arranged in the furnace. A few coals

Fig. 162.



are now applied to the farther end of the tube, so as to decompose a portion of the bicarbonate of soda, the remainder of the carbonate as well as the other part of the tube being protected from the heat by a screen *s*. The current of carbonic acid thus produced is intended to expel all the air from the apparatus. In order to ascertain that this object, on which the success of the whole operation depends, is accomplished, the delivery-tube is depressed under the level of a mercurial trough, and the gas, which is evolved, collected in a test-tube filled with concentrated potassa-solution. If the gas be perfectly absorbed, or, after the introduction of a considerable quantity, only a minute bubble be left, the air may be considered as expelled. The next step is to fill a graduated glass-jar two-thirds with mercury and one-third with a strong solution of potassa, and to invert it over the delivery-tube, as represented in fig. 162.

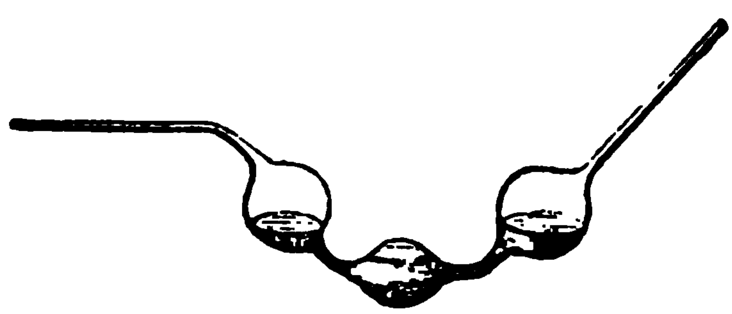
This done, fire is applied to the tube, commencing at the front end, and gradually proceeding to the closed extremity, which yet contains some undecomposed bicarbonate of soda. This, when the fire at length reaches it, yields up carbonic acid, which chases forward the nitrogen lingering in the tube. The carbonic acid generated during the combustion is wholly absorbed by the potassa in the jar, and nothing is left but the nitrogen. When the operation is at an end, the jar, with its contents, is transferred to a vessel of water, and the volume of the nitrogen read off. This is properly corrected for temperature, pressure, and aqueous vapour, and its weight determined by calculation. When the operation has been very successful, and all precautions minutely observed, the result still leaves an error in excess, amounting to 0·8 or 0·5 per cent., due to the residual air of the apparatus, or that condensed into the pores of the protoxide of copper.

A most elegant process for estimating nitrogen in all organic compounds *except those* containing the nitrogen in the form of nitrous, hyponitric

tric acids, has been put into practice by MM. Will and Varrentrapp. When non-azotized organic substance is heated to redness with a large excess of ydrate of potassa or soda, it suffers complete and speedy combustion at the pense of the water of the hydrate, the oxygen combining with the carbon the organic matter to carbonic acid, which is retained by the alkali, while hydrogen, together with that of the substance, is disengaged, sometimes union with a little carbon. The same change happens when nitrogen is esent, but with this addition: the whole of the nitrogen thus abandoned mbines with a portion of the liberated hydrogen to form ammonia. It is, ident, therefore, that if this experiment be made on a weighed quantity matter, and circumstances allow the collection of the whole of the ammonia us produced, the proportion of nitrogen can be easily calculated.

An intimate mixture is made of 1 part caustic soda, and 2 or 3 parts quick-me, by slaking lime of good quality with the proper proportion of strong ustic soda, drying the mixture in an iron vessel, and then heating it to trong redness in an earthen crucible. The ignited mass is rubbed to powder a warm mortar, and carefully preserved from the air. The lime is useful many ways: it diminishes the tendency to deliquescence of the alkali, fa-ilitates mixture with the organic substance, and prevents fusion and lique-action. A proper quantity of the substance to be analyzed, from 5 to 10 rains namely, is dried and accurately weighed out; this is mixed in a warm orcelain mortar with enough of the soda-lime to fill two-thirds of an ordi-ary combustion-tube, the mortar being rinsed with a little more of the lkaline mixture, and, lastly, with a small quantity of powdered glass, which ompletely removes everything adherent to its surface; the tube is then filled within an inch of the open end with the lime-mixture, and arranged in he chauffer in the usual manner. The ammonia is collected in a little ap-paratus of three bulbs (fig. 163) containing moderately strong hydrochloric

Fig. 163.



id, attached by a cork to the combustion-tube. Matters being thus ad-usted, fire is applied to the tube commencing with the anterior extremity. hen ignited throughout its whole length, and when no more gas issues from e apparatus, the point of the tube is broken, and a little air drawn through e whole. The acid liquid is then emptied into a capsule, the bulbs rinsed to the same, first with a little alcohol, and then repeatedly with distilled ater; an excess of pure bichloride of platinum is added, and the whole vaporated to dryness in a water-bath. The dry mass, when cold, is treated ith a mixture of alcohol and ether, which dissolves out the superfluous bi-hloride of platinum, but leaves untouched the yellow crystalline double hloride of platinum and ammonium. The latter is collected upon a small eighed filter, washed with the same mixture of alcohol and ether, dried at 12° (100°C), and weighed; 100 parts correspond to 6·272 parts of nitrogen; r, the salt with its filter may be very carefully ignited, and the filter burned a platinum crucible, and the nitrogen reckoned from the weight of the pongy metal, 100 parts of that substance corresponding to 14·18 parts of itrogen. *The former plan is to* be preferred in most cases.

Bodies very rich in nitrogen, as urea, must be mixed with about an eq quantity of pure sugar, to furnish incondensible gas, and thus diminish violence of the absorption which otherwise occurs; and the same precaut must be taken, for a different reason, with those which contain little or hydrogen.

A modification of this process has been lately suggested by M. Péli which is very convenient if a large number of nitrogen-determinations to be made. By this plan the ammonia, instead of being received in hyd chloric acid, is conducted into a known volume (from ½ to 1 cubic inch) a standard solution of sulphuric acid, contained in the ordinary nitrog bulbs. After the combustion is finished, the acid containing the ammoni poured out into a beaker, coloured with a drop of tincture of litmus, then neutralized with a standard solution of soda in water or of lime sugar-water, the point of neutralization becoming perceptible by the sud appearance of a blue tint. The lime-solution is conveniently poured from the graduated glass-tube, fig. 186, described under the head of alk metry (page 227). The volume of lime-solution necessary to neutralise same amount of acid, which is used for condensing the ammonia, has been ascertained by a preliminary experiment, it is evident that the dif ence of the quantities used in the two experiments gives the ammonia lected during the combustion in the acid; the amount of nitrogen may be calculated. If, for instance, an acid be prepared, containing 20 gr of pure hydrated sulphuric acid (SO_3,HO) in 1,000 grain-measures — grain-measures of this acid — the quantity introduced into the bulbs — respond to 1·88 grains of ammonia, or 1·14 grains of nitrogen. The a line solution is so graduated that 1,000 grain-measures will exactly neu lize the 200 grain-measures of the standard acid. If we now find that acid partly saturated with the ammonia, disengaged during the combus of a nitrogenous substance, requires only 700 grain-measures of the alka solution, it is evident that $\frac{200 \times 300}{1000} = 60$ grain-measures were satur by the ammonia, and the quantity of nitrogen is obtained by the propor $200 : 1{\cdot}14 = 60 : x$, wherefrom $x = \frac{1{\cdot}14 \times 60}{200} = 0{\cdot}342$ grains of nitrog

Estimation of Sulphur in organic compounds.—When bodies of this c containing sulphur are burned with protoxide of copper, a small tube c taining binoxide of lead must be interposed between the chloride of calci tube and the potass-apparatus to retain any sulphurous acid which may formed. It is better, however, to use chromate of lead in such cases. proportion of sulphur is determined by oxidizing a known weight of the s stance by strong nitric acid, or by fusion in a silver vessel with ten or tw times its weight of pure hydrate of potassa and half as much nitre. sulphur is thus converted into sulphuric acid, the quantity of which can determined by dissolving the fused mass in water, acidulating with ni acid, and adding a salt of baryta. Phosphorus is, in like manner, oxid to phosphoric acid, the quantity of which is determined by precipitation combination with sesquioxide of iron, or otherwise.

Estimation of Chlorine.—The case of a volatile liquid containing chlo is of most frequent occurrence, and may be taken as an illustration of general plan of proceeding. The combustion with protoxide of cop must be very carefully conducted, and two or three inches of the ante portion of the tube kept cool enough to prevent volatilization of the chlo of copper into the chloride of calcium tube. Chromate of lead is m better for the purpose. The chlorine is correctly determined by placi small weighed bulb of liquid in a combustion-tube, which is afterw

led with fragments of pure quick-lime. The lime is brought to a red-at, and the vapour of the liquid driven over it, when the chlorine dis-aces oxygen from the lime, and gives rise to chloride of calcium. When ld, the contents of the tube are dissolved in the dilute nitric acid, filtered, d the chlorine precipitated by nitrate of silver.

EMPIRICAL AND RATIONAL FORMULÆ.

A chemical formula is termed *empirical* when it merely gives the simplest ssible expression of the composition of the substance to which it refers. *rational* formula, on the contrary, aims at describing the exact composition *one equivalent*, or *combining proportion* of the substance, by stating the solute number of equivalents of each of its elements essential to that ject, as well as the mere relations existing between them. The empirical rmula is at once deduced from the analysis of the substance, reckoned to 0 parts; the rational requires in addition a knowledge of its combining antity, which can only be obtained by direct experiment, by synthesis, or the careful examination of one or more of its most definite compounds. rther, the rational may either coincide with the empirical formula, or it y be a multiple of the latter.

Thus, the composition of acetic acid is expressed by the formula $C_4H_3O_3$, ich exhibits the simplest relations of the three elements, and at the same e expresses the quantities of these, in equivalents, required to make up *equivalent* of acetic acid; hence, it is both empirical and rational. On other hand, the empirical formula of crystallized kinic acid is $C_7H_6O_6$, ile its rational formula, determined by its capacity of saturation, is double, $C_{14}H_{12}O_{12}$, otherwise written $C_{14}H_{11}O_{11},HO$. In like manner, the empi-l formula of the artificial alkaloids *furfurine* and *amarine* are respectively H_6NO_3 and $C_{21}H_9N$. The equivalents of these substances, that is to say, quantities required to form neutral salts with one equivalent of any well-ed monobasic acid, will, however, be expressed by the formulæ $C_{30}H_{12}O_6$ and $C_{42}H_{18}N_2$; hence these latter deserve the name of rational.

The deduction of an empirical formula from the ultimate analysis is very y; the case of sugar, already cited, may be taken as an example. This tains, according to the analysis, in 100 parts

Carbon	41·98
Hydrogen	6·43
Oxygen	51·59
	100·00

If each of these quantities be divided by the equivalent of the element, quotients will express *in equivalents* the relations existing between them; se are afterwards reduced to their simplest expression. This is the only t of the calculation attended with any difficulty; if the numbers were rigidly ect, it would only be necessary to divide each by the greatest divisor mon to the whole; as they are, however, only approximative, something of necessity left to the judgment of the experimenter, who is obliged to more indirect means.

$$\frac{41·98}{6}=6·99;\ 6·43;\ \frac{51·59}{8}=6·44,$$

or 699 eq. carbon, 643 eq. hydrogen, and 644 eq. oxygen.

It will be evident, in the first place, that the hydrogen and oxygen are sent in the proportions to form water, or as many equivalents of one as the other. *Again, the equivalents* of carbon and hydrogen are nearly in

Bodies very rich in nitr… $C_{18}H_{11}O_{11}$ appears likely
quantity of pure sugar, … is admissible, by recko…
violence of the absorpt… with the numbers given by the …
must be taken, for a … difference falls fairly in directi…
hydrogen. … what may be termed a good expe…

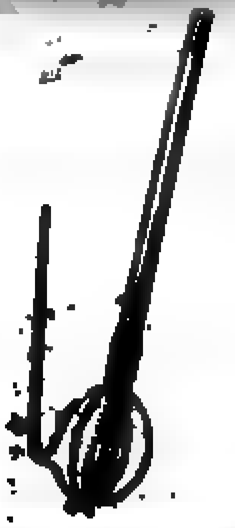
A modification of … deficiency in the carbon, and not mo…
which is very conv… hydrogen.
to be made. By t…
chloric acid, is c… .... $6 \times 12 = 72$
a standard solu… .... 11 eq. $= 11$
bulbs. After t… .... $8 \times 11 = 88$
poured out in… 171
then neutrali…
sugar-water, $171 : 72 = 100 : 42{\cdot}11$
appearance $171 : 11 = 100 : 6{\cdot}43$
from the g… $171 : 88 = 100 : 51{\cdot}46$

metry (pa… Organic acids and salt-radicals have their proper equivalents …
same am… commonly determined by an analysis of their lead- and silver-salts, by
been asc… them better with suitable precautions in a thin porcelain capsule, an…
ence of … the weight of the protoxide of lead or metallic silver left behind.
lected … proportion of lead be mixed with globules of reduced metal, the qua…
be cal… the latter must be ascertained by dissolving away the oxide by acet…
of pu… the lead-salt may be converted into sulphate, and the silver-co…
grain … or the chloride, and both metals thus estimated. An organic base, on …
resp… a salt, or a basic, has its equivalent fixed by the observation of the …
line … of a mineral acid, or an inorganic salt-radical, required to form w…
… combination having the characters of neutrality.

DETERMINATION OF THE DENSITY OF VAPOURS.

The determination of the specific gravity of the vapour of a vola… stance is frequently a point of great importance, in… as it gives the means, in conjunction with the anal… representing the constitution of the substance by … in a gaseous state. The following is a sketch of … of operation usually followed: — A light glass gl… 164, about three inches in diameter, is taken, and … softened and drawn out in the blowpipe-flame, a… sented in the figure, this is accurately weighed. … one hundred grains of the volatile liquid are the… duced, by gently warming the globe and dipping t… into the liquid, which is then forced upwards by t… sure of the air as the vessel cools. The globe … firmly attached by wire to a handle, in such a man… it may be plunged into a bath of boiling water or … oil, and steadily held with the point projecting u… The bath must have a temperature considerabl… that of the boiling-point of the liquid. The latter … rapidly converted into vapour, which escapes by t… row orifice, chasing before it the air of the globe.

Fig. 164.



… the issue of vapour has wholly ceased, and the temperature of the bat… fully observed, appears pretty uniform, the open extremity of the … hermetically sealed by a small blowpipe-flame. The globe is remov… the bath, suffered to cool, cleansed if necessary, and weighed, aft… the neck is broken off beneath the surface of water which has bee… and cooled out of contact of air, or better, mercury. The liquid en… globe, and, if the expulsion of the air by the vapour has been compl…

... an air-bubble is left, whose volume can be easily ascertained ... liquid from the globe into a jar graduated to cubic inches, ...-filling the globe, and repeating the same observation. The ... the vessel is thus at the same time known; and these are all the ...uired. An example will render the whole intelligible.

Determination of the density of the vapour of Acetone.

Capacity of globe	31·61 cubic inches
Weight of globe filled with dry air at 52° (11°·11C) and 30·24 inches barometer...........................	2070·88 grains.
Weight of globe filled with vapour at 212° (100°C) temp. of the bath at the moment of sealing the point, and 30·24 inches barometer	2076·81 grains.
Residual air, at 45° (7°·22C), and 30·24 inches barometer..	0·60 cubic inch.

...1 cub. inches of air at 52° and 30·24 in bar. = 32·36 cub. inches at 60° (15°·C) and 30 inch. bar., weighing...............................10·035 grains.
...ce, weight of empty globe..............2070·88—10·035 = 2060·845 grains.

... c. inch of air at 45° = 0·8 c. inch at 212°; weight of do. by calculation = 0·191 grain.

...61—0·8 = 30·81 cubic inches of vapour at 212° and 30·24 in. bar., which, ... *the supposition that it could bear cooling to* 60° *without liquefaction*, would, ... that temperature, and under a pressure of 30 inch. bar., become reduced ... 24·18 cubic inches.

...ce,

Weight of globe and vapour..............................	2076·810 grains.
,, residual air..	0·191
	2076·619
Weight of globe..	2060·845
Weight of the 24·18 cubic inches of vapour.............	15·774
...sequently, 100 cubic inches of such vapour must weigh..	65·23
... cubic inches of air, under similar circumstances, weigh	31·01

$\frac{65 \cdot 23}{31 \cdot 01} = 2 \cdot 103$, the specific gravity of the vapour in question, air being unity.

... the foregoing statement a correction has been, for the sake of simpli... ...omitted, which, in very exact experiments, must not be lost sight of, ...e expansion and change of capacity of the glass globe by the elevated ...ature of the bath. The density so obtained will be always on this ... a little too high.

...rror to which the mercurial thermometer is, at high temperatures, ...ends in the *opposite direction*.

It is easy to compare the actual specific gravity of the vapour found in the manner above described with the theoretical specific gravity deduced from the formula of the substance:—

The formula of acetone is C_3H_6O. In combining volumes this is represented by 3 vols. of the hypothetical vapour of carbon, 3 vols. of hydrogen, and half a volume of oxygen. Or the weight of the unit of volume of acetone-vapour will be equal to three times the specific gravity of carbon-vapour, three times that of hydrogen, and one-half that of oxygen added together, one volume of the compound vapour containing $6\frac{1}{2}$ volumes of its components:

3 vols. hypothetical vapour of carbon................	$0{\cdot}4183 \times 3 = 1{\cdot}2549$
3 vols. hydrogen	$0{\cdot}0693 \times 3 = 0{\cdot}2079$
$\frac{1}{2}$ vol. oxygen...	$= 0{\cdot}5528$
Theoretical specific gravity	$2{\cdot}0156$

SECTION I.

ZOTIZED BODIES OF THE SACCHARINE AND AMYLACEOUS GROUP.

SUGAR, STARCH, GUM, LIGNIN, AND ALLIED SUBSTANCES.

members of this remarkable and very natural group present several ting cases of isomerism. They are characterized by their feeble le to enter into combination, and also by containing, with perhaps one ion, oxygen and hydrogen in the proportions to form water.

Table of Saccharine and Amylaceous Substances.

Cane-sugar, crystallized	$C_{24}H_{22}O_{22}$
Cane-sugar, in combination	$C_{24}H_{18}O_{18}$
Grape-sugar, crystallized	$C_{24}H_{28}O_{28}$
Grape-sugar, in combination	$C_{24}H_{21}O_{21}$
Milk-sugar, crystallized	$C_{24}H_{24}O_{24}$
Milk-sugar, in combination	$C_{24}H_{19}O_{19}$
Sugar from *Secale cornutum*	$C_{24}H_{26}O_{26}$
Mannite	$C_6H_7O_6$
Starch, unaltered, dried at 212° (100°C)	$C_{24}H_{20}O_{20}$
Amidin, or gelatinous starch	$C_{24}H_{20}O_{20}$
Dextrin, or gummy starch	$C_{24}H_{20}O_{20}$
Starch from *Cetraria Islandica*	$C_{24}H_{20}O_{20}$
Inulin	$C_{24}H_{21}O_{21}$
Gum-Arabic	$C_{24}H_{22}O_{22}$
Gum-tragacanth	$C_{24}H_{20}O_{20}$
Lignin, or cellulose	$C_{24}H_{20}O_{20}$

E-SUGAR; ORDINARY SUGAR, $C_{24}H_{22}O_{22}$.—This most useful substance is in the juice of many of the grasses, in the sap of several forest-trees, root of the beet and the mallow, and in several other plants. It is ted most easily and in greatest abundance from the sugar-cane, culti- for the purpose in many tropical countries. The canes are crushed en rollers, and the expressed juice suffered to flow into a large vessel it is slowly heated nearly to its boiling-point. A small quantity of te of lime mixed with water is then added, which occasions the separa- f a coagulum consisting chiefly of earthy phosphates, waxy matter, a ar albuminous principle, and mechanical impurities. The clear liquid ated from the coagulum thus produced is rapidly evaporated in open heated by a fierce fire made with the crushed canes of the preceding dried in the sun and preserved for the purpose. When sufficiently ntrated the syrup is transferred to a shallow vessel, and left to crys- , during which time it is frequently agitated in order to hasten the e and hinder the formation of large crystals. It is, lastly, drained

from the dark uncrystallizable syrup, or *molasses*, and sent into co
under the name of *raw* or *Muscovado* sugar. The refining of this cru
duct is effected by re-dissolving it in water, adding a quantity of alb
the shape of serum of blood or white of egg, and sometimes a litt
water, and heating the whole to the boiling-point; the albumen coa
and forms a kind of net-work of fibres, which inclose and separate f
liquid all mechanically suspended impurities. The solution is decolo
filtration through animal charcoal, evaporated to the crystallizing-p
put into conical earthen moulds, where it solidifies, after some ti
confusedly-crystalline mass, which is drained, washed with a litt
syrup, and dried in a stove; the product is ordinary *loaf-sugar*. W
crystallization is allowed to take place quietly and slowly, *sugar-c*
sults, the crystals under these circumstances acquiring large vol
regular form. The evaporation of the decolorized syrup is best co
in strong close boilers exhausted of air; the boiling-point of the
reduced in consequence from 230° (110°C) to 150° (65°·5C) or be
and the injurious action of the heat upon the sugar in great meas
vented. Indeed, the production of molasses in the rude colonial man
is chiefly the result of the high and long-continued heat applied to t
juice, and might be almost entirely prevented by the use of vacu
the product of sugar being thereby greatly increased in quantity, a
improved in quality as to become almost equal to the refined article

In many parts of the continent of Europe sugar is manufactured o
scale from beet-root, which contains about 8 per cent. of that substa
process is far more complicated and troublesome than that just d
and the product much inferior. When refined, however, it is scarc
distinguished from the preceding. The inhabitants of the Western S
America prepare sugar in considerable quantity from the sap of th
maple, *Acer saccharinum*, which is common in those parts. The tree
in the spring by boring a hole a little way into the wood, and ins
small spout to convey the liquid into a vessel placed for its receptic
is boiled down in an iron pot, and furnishes a coarse sugar, which
wholly employed for domestic purposes, but little finding its way i
merce.

Pure sugar slowly separates from a strong solution in large, tra
colourless crystals, having the figure of a modified oblique rhomb
It has a pure, sweet taste, is very soluble in water, requiring for
only one-third of its weight in the cold, and is also dissolved by alc
with more difficulty. When moderately heated it melts, and sol
cooling to a glassy amorphous mass, familiar under the name of *bar*
at a higher temperature it blackens and suffers decomposition; and
effect is produced, as already remarked, by long-continued boilin
aqueous solution, which loses its faculty of crystallizing and acquir
The crystals have a specific gravity of 1·6, and are unchanged in t

The deep brown soluble substance called *caramel*, used for colourin
and other purposes, is a product of the action of heat upon cane-s
contains $C_{24}H_{18}O_{18}$, and is isomeric with cane-sugar in combination.

The following is the composition assigned to the principal comp
cane-sugar by M. Péligot, who has devoted much attention to the s

Crystallized cane-sugar	$C_{24}H_{18}O_{18}+4HO$
Compound of sugar with common salt	$C_{24}H_{18}O_{18}+NaCl+$
Compound of sugar with baryta	$C_{24}H_{18}O_{18}+2BaO+$
Compound of sugar with lime	$C_{24}H_{18}O_{18}+2CaO+$
Compound of sugar with protoxide of lead	$C_{24}H_{18}O_{18}+4PbO$

[1] Ann. Chim. et Phys. lxvii. 113.

pounds with baryta and lime are prepared by digesting sugar at eat with the hydrates of the earths. The lime-compound has a e, and is more soluble in cold water than in hot. Both are readily d by carbonic acid, crystals of carbonate of lime being occasioned. The combination with protoxide of lead is prepared by mix- with a solution of acetate of lead, adding excess of ammonia, and white insoluble product out of contact with air. The compound non salt is crystallizable, soluble, and deliquescent.

UGAR; GLUCOSE; SUGAR OF FRUITS, $C_{24}H_{28}O_{28}$. — This variety of ry abundantly diffused through the vegetable kingdom; it may be in large quantity from the juice of sweet grapes, and also from which it forms the solid crystalline portion, by washing with cold hich dissolves the fluid syrup. It may also be prepared by arti- difying cane-sugar, starch, and woody fibre, by processes presently ribed. The appearance of this substance, to an enormous extent, e, is the most characteristic feature of the disease called *diabetes*. ugar is easily distinguished by several important peculiarities from r: it is much less sweet, and less soluble in water, requiring 1½ he cold liquid for solution. Its mode of crystallisation is also different; instead of forming, like cane-sugar, bold, distinct crys- arates from its solutions in water and alcohol in granular warty hich but seldom present crystalline faces. When pure, it is nearly hen heated, it melts, and loses 4 eq. of water, and at a higher re blackens and suffers decomposition. Grape-sugar combines ulty with lime, baryta, and oxide of lead, and is converted into a black substance when boiled with solution of caustic alkali, by e-sugar is but little affected. It dissolves, on the contrary, in of vitriol without blackening, and gives rise to a peculiar com- l, whose baryta-salt is soluble. Cane-sugar is, under these cir- s, instantly changed to a black mass resembling charcoal.

lutions of cane and grape-sugar are mixed with two separate por- lution of sulphate of copper, and caustic potassa added in excess ep blue liquids are obtained, which, on being heated, exhibit dif- racters; the one containing cane-sugar is at first but little altered; antity of red powder falls after a time, but the liquid long retains it: with the grape-sugar, on the other hand, the first application rows down a copious greenish precipitate, which rapidly changes and eventually to dark red, leaving a nearly colourless solution. excellent test for distinguishing the two varieties of sugar, or dis- n admixture of grape with cane-sugar.

ugar unites with common salt, forming a soluble compound of aline taste, which crystallizes in a regular and beautiful manner.

Compounds of Grape-sugar, according to Péligot.

grape-sugar dried in the air	$C_{24}H_{21}O_{21} + 7HO$
dried at 266° (130°C)	$C_{24}H_{21}O_{21} + 3HO$
of grape-sugar with common salt	$C_{24}H_{21}O_{21} + NaCl + 5HO$
dried at 266° (130°C)	$C_{24}H_{21}O_{21} + NaCl + 2HO$
of grape-sugar with baryta	$C_{24}H_{21}O_{21} + 3BaO + 7HO$
of grape-sugar with lime	$C_{24}H_{21}O_{21} + 3CaO + 7HO$
of grape-sugar with protoxide of lead	$C_{24}H_{21}O_{21} + 6PbO$

ccharic Acid, $C_{24}H_{20}O_{20},SO_3$. — Melted grape-sugar is cautiously h concentrated sulphuric acid, the product dissolved in water, and l with carbonate of baryta; sulphate of baryta is formed together uble *sulphosaccharate* of that earth, from which the acid itself

may be afterwards eliminated. It is a sweetish liquid, forming a variety of soluble salts, and very prone to decompose into sugar and sulphuric acid.

Action of dilute Acids upon Sugar.—Cane-sugar dissolved in dilute sulphuric acid is gradually but completely converted, at the common temperature of the air, into grape-sugar. The same solution, when long boiled, yields a brownish-black and nearly insoluble substance, which is a mixture of two distinct bodies, one having the appearance of small shining scales, and the other that of a dull brown powder. The first, called by Boullay and Malaguti *ulmin*, and by Liebig *sacchulmin*, is insoluble in ammonia and alkalis; the second, *ulmic acid*, the *sacchulmic acid* of Liebig, dissolves freely, yielding dark brown solutions precipitable by acids. By long-continued boiling with water, sacchulmic acid is converted into sacchulmin. Both these substances have the same composition, expressed by the empirical formula C_8HO. Hydrochloric acid in a dilute state, produces the same effects.[1]

Action of Alkalis upon Sugar.—When lime or baryta is dissolved in a solution of grape-sugar, and the whole left to itself several weeks in a closed vessel, the alkaline reaction will be found to have disappeared from the formation of an acid substance. By mixing this solution with basic acetate of lead, a voluminous white precipitate is obtained, which, when decomposed by sulphuretted hydrogen, yields sulphide of lead, and the new acid, to which the term *kalisaccharic* or *glucic* is applied. Glucic acid is very soluble and deliquescent, has a sour taste and acid reaction: its salts, with the exception of that containing protoxide of lead, are very soluble. It contains C_8H... When grape-sugar is heated in a strong solution of potassa, soda, or baryta, the liquid darkens, and at length assumes a nearly black colour. The addition of an acid then gives rise to a black flocculent precipitate of a substance called *melasinic* acid, containing $C_{24}H_{10}O_{10}$. Cane-sugar long-boiled with alkalis undergoes the same changes, being probably first converted into grape-sugar.

SUGAR FROM ERGOT OF RYE.—This variety of sugar, extracted by alcohol from the ergot, crystallizes in transparent colourless prisms, which have a sweet taste, and are very soluble in water. It differs from cane-sugar in not reducing the acetate of copper when boiled with a solution of that substance. It contains $C_{24}H_{26}O_{26}$.

SUGAR OF DIABETES INSIPIDUS.—A substance having the other properties of a sugar, but destitute of sweet taste, has been described by M. Thénard as having been obtained from the above-mentioned source. It was capable of furnishing alcohol by fermentation, and of suffering conversion into grape-sugar by dilute sulphuric acid. Its composition is unknown.

LIQUORICE-SUGAR; GLYCYRRHIZIN.—The root of the common liquorice yields a large quantity of a peculiar sweet substance, which is soluble in water, but refuses to crystallize; it is remarkable for forming with acids compounds which have but sparing solubility. Glycyrrhizin cannot be made to ferment. The formula of this substance is not definitely settled.

SUGAR OF MILK; LACTIN, $C_{24}H_{24}O_{24}$.—This curious substance is an important constituent of milk; it is obtained in large quantities by evaporating *whey* to a syrupy state, and purifying the lactin, which slowly crystallizes, by animal charcoal. It forms white, translucent, four-sided prisms, of ...

[1] Under the names *ulmin* and *ulmic acid* (*humin* and *humic acid*, *crenic* and *apocrenic* acid) have been confounded a number of brown or black uncrystallizable substances, produced by the action of powerful chemical agents upon sugar, lignin, &c., or generated by the putrefactive decay of vegetable fibre. Common garden mould, for example, treated with dilute solution of caustic potassa, yields a deep brown solution, from which acids precipitate a flocculent, brown substance, having but a slight degree of solubility in water. This is generally called *ulmic* or *humic* acid, and its origin ascribed to the reaction of the alkali on the ulmin or *humus* of the soil. It is known that these bodies differ exceedingly in composition, and are too indefinite to admit of ready investigation.

dness. It is slow and difficult of solution in cold water, requiring for t purpose 5 or 6 times its weight; it has a feeble sweet taste, and in the d state feels gritty between the teeth. When heated, it loses water, and at igh temperature blackens and decomposes. Milk-sugar forms several comnds with protoxide of lead, and is converted into grape-sugar by boiling a dilute mineral acids. It is not directly fermentable, but can be made, er particular circumstances, to furnish alcohol.

ANNA-SUGAR; MANNITE, $C_6H_7O_6$ or $C_{12}H_{14}O_{12}$.—This is the chief compot of *manna*, an exudation from a species of ash; it is also found in the e of certain other plants, and in several sea-weeds, and may be formed ficially from ordinary sugar by a peculiar kind of fermentation. It is prepared by treating manna with boiling alcohol, and filtering the soluwhilst hot; the mannite crystallizes on cooling in tufts of slender colourneedles. It is fusible by heat without loss of weight, is freely soluble ater, possesses a powerfully sweet taste, and has no purgative properties. nite refuses to ferment. This substance combines with sulphuric acid, ng rise to a new acid, the composition of which is not yet definitely blished. It is likewise acted on by concentrated nitric acid. The product his action will be noticed farther on. The substance formerly described ushroom-sugar is merely mannite.

TARCH; FECULA.—This is one of the most important and widely diffused he vegetable proximate principles, being found to a greater or less extent very plant. It is most abundant in certain roots and tubers, and in soft ns: seeds often contain it in large quantity. From these sources the ls can be obtained by rasping or grinding to pulp the vegetable structure, washing the mass upon a sieve, by which the torn cellular tissue is reed, while the starch passes through with the liquid, and eventually settles n from the latter as a soft, white, insoluble powder, which may be washed a cold water, and dried with very gentle heat. Potatoes treated in this nner yield a large proportion of starch. Starch from grain may be pred in the same manner, by mixing the meal with water to a paste, and hing the mass upon a sieve: a nearly white, insoluble substance called ten or *glutin* remains behind, which contains a large proportion of nitrogen. glutin of wheat-flour is extremely tenacious and elastic. The value of d as an article of food greatly depends upon this substance. Starch from in is commonly manufactured on the large scale by steeping the material water for a considerable period, when the lactic acid, always developed ler such circumstances from the sugar of the seed, disintegrates, and in t dissolves the azotized matter, and greatly facilitates the mechanical aration of that which remains. A still more easy and successful process lately been introduced, in which a very dilute solution of caustic soda, taining about 200 grains of alkali to a gallon of liquid is employed with same view. Excellent starch is thus prepared from rice. Starch is insole in cold water, as indeed its mode of preparation sufficiently shows; it qually insoluble in alcohol and other liquids which do not effect its deposition. To the naked eye it presents the appearance of a soft, white, d often glistening powder; under the microscope it is seen to be altogether titute of crystalline structure, but to possess, on the contrary, a kind of ganization, being made up of multitudes of little rounded transparent dies, upon each of which a series of depressed parallel rings surrounding entral spot or hilum, may often be traced. The starch-granules from difent plants vary both in magnitude and form; those from the *Canna coc-ea*, or *tous les mois*, and potato being largest; and those from wheat, and cereals in general, very much smaller. The figure on the next page g. 165) will serve to convey an idea of the appearance of the granules of tato-starch, highly magnified.

Fig. 168.

When a mixture of starch and water i to near the boiling-point of the latter, the burst and disappear, producing, if the p of starch be considerable, a thick gelati very slightly opalescent from the shred fine membrane, the envelope of each granule. By the addition of a large qu water, this gelatinous starch, or amidi so far diluted as to pass in great measu filter-paper. It is very doubtful, how far the substance itself is really soluble at least when cold; it is more likely to suspended in the liquid in the form of transparent, insoluble jelly, of extrem Gelatinous starch, exposed in a thin dry atmosphere, becomes converted i lowish, horny substance, like gum, wl put into water, again softens and swells.

Thin gelatinous starch is precipitated by many of the metallic lime, baryta, and protoxide of lead, and also by a large addition Infusion of galls throws down a copious yellowish precipitate tannic acid, which re-dissolves when the solution is heated. most characteristic reaction, however, is that with free iodine, w with starch a deep indigo-blue compound, which appears to dissol water, although it is insoluble in solutions containing free acid matter. The blue liquid has its colours destroyed by heat, tem the heat be quickly withdraw, and permanently if the boiling be tinued, in which case the compound is decomposed and the ioc lized. Starch in the dry state, put into iodine-water, acquires black colour.

The unaltered and the gelatinous starch, in a dried state, hav composition, namely, $C_{24}H_{20}O_{20}$; a compound of starch and pr lead was found to contain, when dried at 212° (100°C), $C_{24}H_{20}O_{2}$

Dextrin.—When gelatinous starch is boiled with a small q dilute sulphuric, hydrochloric, or, indeed, almost any acid, it sp its consistency, and becomes thin and limpid, from having suffer sion into a soluble substance, resembling gum, called dextrin.[1] T ment is most conveniently made with sulphuric acid, which ma wards withdrawn by saturation with chalk. The liquid filtere nearly insoluble gypsum may then be evaporated in a water-b ness. The result is a gum-like mass, destitute of crystalline soluble in cold water, and precipitable from its solution by a capable of combining with protoxide of lead.

When the ebullition with the dilute acid is continued for a c period, the dextrin first formed undergoes a farther change, an converted into grape-sugar, which can be thus artificially produc greatest facility. The length of time required for this remarka depends upon the quantity of acid present; if the latter be very necessary to continue the boiling many successive hours, rep water which evaporates. With a larger proportion of acid, the co much more speedy. A mixture of 15 parts potato-starch, 60 p and 6 parts sulphuric acid, may be kept boiling for about four liquid neutralized with chalk, filtered, and rapidly evaporated

[1] From its action on polarised light, twisting the plane of polarization towards the right hand.

:- By digestion with animal charcoal and a second filtration much of colour will be removed, after which the solution may be boiled down to in syrup and left to crystallize; in the course of a few days it solidifies mass of grape-sugar. There is another method of preparing this sub-ce from starch which deserves particular notice. Germinating seeds, buds in the act of development, are found to contain a small quantity peculiar azotized substance, formed at this particular period from the in or vegetable albuminous matter, to which the name *diastase* is given. substance possesses the same curious property of effecting the conver- of starch into dextrin, and ultimately into grape-sugar, and at a much er temperature than that of ebullition. A little infusion of malt, or ger-ated barley, in tepid water, mixed with a large quantity of thick gela-us starch, and the whole maintained at 160° (71°C), or thereabouts, sions complete liquefaction in the space of a few minutes from the pro-tion of dextrin, which in its turn becomes in three or four hours con-ed into sugar. If a greater degree of heat be employed, the diastase is gulated and rendered insoluble and inactive. Very little is known ecting diastase itself; it seems very much to resemble vegetable albumin, has never been got in a state of purity.

he change of starch or dextrin into sugar, whether produced by the on of dilute acid or by diastase, takes place quite independently of the gen of the air, and is unaccompanied by any secondary product. The l takes no direct part in the reaction; it may, if not volatile, be all with-wn without loss after the experiment. The whole affair lies between the ch and the elements of water; a fixation of the latter occuring in the r product, as will be seen at once on comparing their composition. The ar, in fact, so produced, very sensibly exceeds in weight the starch em-yed. Dextrin itself has exactly the same composition as the original ch.

Dextrin is used in the arts as a substitute for gum; it is sometimes made the manner above described, but more frequently by heating dry potato-rch to 400° (204°·5C), by which it acquires a yellowish tint and becomes able in cold water. It is sold in this state under the appellation of *British m.*

Starch is an important article of food, especially when associated, as in inary meal, with albuminous substances. Arrow-root, and the fecula of *Canna coccinea*, are very pure varieties, employed as articles of diet; ow-root is obtained from the *Maranta arundinacea*, cultivated in the West lies; it is with difficulty distinguished from potato-starch. *Tapioca* is pared from the root of the *Iatropha manihot*, being thoroughly purified n its poisonous juice. *Cassava* is the same substance modified while st by heat. *Sago* is made from the soft central portion of the stem of a m-tree.

STARCH FROM ICELAND MOSS. — The lichen called *Cetraria Islandica*, puri-d by a little cold solution of potassa from a bitter principle, yields when iled in water a slimy and nearly colourless liquid, which gelatinizes on aling, and dries up to a yellowish amorphous mass, which does not dissolve cold water, but merely softens and swells. A solution of this substance warm water is not affected by iodine, although the jelly, on the contrary, rendered blue. It is precipitated by alcohol, acetate of lead, and infusion galls, and is converted by boiling with dilute sulphuric acid into grape-gar. According to Mulder, linen-starch likewise contains $C_{24}H_{20}O_{20}$. The ly from certain *algæ*, as that of Ceylon, and the so-called *Carragheen moss*, osely resembles the above.

INULIN. — This substance, which differs from common starch in some im-rtant particulars, is found in the root of the *Inula helenium*, the Helianthus

tuberosus, the *dahlia*, and several other plants; it may be easily obtained by washing the rasped root on a sieve, and allowing the inulin to settle down from the liquid; or by cutting the root into thin slices, boiling these in water, and filtering while hot; the inulin separates as the solution cools. It is a white, amorphous, tasteless substance, nearly insoluble in cold water, but freely dissolved by the aid of heat; the solution is precipitated by alcohol, but not by acetate of lead or infusion of galls. Iodine communicates a brown colour. Inulin has been analyzed by Mr. Parnell, who finds it to contain, when dried at 212° (100°C), $C_{24}H_{21}O_{21}$.

GUM. — *Gum-Arabic*, which is the produce of an acacia, may be taken as the most perfect type of this class of bodies. In its purest and finest condition, it forms white or slightly yellowish irregular masses, which are destitute of crystalline structure, and break with a smooth conchoidal fracture. It is soluble in cold water, forming a viscid, adhesive, tasteless solution, from which the pure soluble gummy principle, or *arabin*, is precipitated by alcohol and by basic acetate of lead, but not by the neutral acetate. Arabin is composed of $C_{24}H_{22}O_{22}$, and is consequently isomeric with crystallized cane-sugar.

Mucilage, so abundant in linseed, in the roots of the mallow, in *salep*, the fleshy root of *Orchis mascula*, and in other plants, differs in some respects from the foregoing, although it agrees in the property of dissolving in cold water. The solution is less transparent than that of gum, and is precipitated by neutral acetate of lead. *Gum tragacanth* is chiefly composed of a kind of mucilage to which the name *bassorin* has been given, and which refuses to dissolve in water, merely softening and assuming a gelatinous aspect. It is dissolved by caustic alkali. *Cerasin* is the term given to the insoluble portion of the gum of the cherry-tree; it resembles bassorin. The composition of these various substances has been carefully examined by Dr. Schmidt, who finds that it closely agrees with that of starch. Mucilage invariably contains hydrogen and oxygen in the proportion in which they form water, and when treated with acid, yeild grape-sugar.

Pectin, or the jelly of fruits, is, in its physical properties, closely allied to the foregoing bodies. It may be extracted from various vegetable juices by precipitation by alcohol. It forms, when moist, a transparent jelly, soluble in water, and tasteless, which dries up to a translucent mass. It is to this substance that the firm consistence of currant and other fruit jellies is to be ascribed. According to M. Fremy, the composition of pectin is $C_{64}H_{40}O_{56}$. By ebullition with water and with dilute acids it is changed into two isomeric modifications, to which the names *parapectin* and *metapectin* have been given. In contact with bases, these three substances become converted into *pectic acid*, which, except that it possesses feeble acid properties, and is insoluble in water, resembles in the closest manner pectin itself. By long boiling with solution of caustic alkali, a further change is produced, and a new acid, the *metapectic*, developed, which does not gelatinize. The salts of these two acids are incapable of crystallizing. Their composition is represented by the following formulæ:—

Pectic acid	$2HO,C_{32}H_{20}O_{28}$
Metapectic acid	$2HO,C_{24}H_{15}O_{21}$

Much doubt still exists respecting the composition of the various bodies of the pectin-series; they do not appear, from the analyses yet made, to

[1] The precipitate produced by sub-salts of lead is a compound of arabine and oxide of $C_{24}H_{22}O_{22}+2PbO$. By the action of very dilute sulphuric acid arabine is slowly changed to dextrine, and by prolonged contact into glucose. Nitric acid decomposes gum and produces first mucic and ultimately oxalic acid.—R. B.

oxygen and hydrogen in equal equivalents, and consequently scarcely ng to the starch-group.

IGNIN; CELLULOSE.—This substance constitutes the fundamental mate- of the structure of plants; it is employed in the organization of cells, vessels of all kinds, and forms a large proportion of the solid parts of y vegetable. It must not be confounded with *ligneous* or *woody tissue*, ch is in reality cellulose, with other substances superadded, which encrust walls of the original membraneous cells, and confer stiffness and inflex- ty. Thus woody tissue, even when freed as much as possible from uring matter and resin by repeated boiling with water and alcohol, ds on analysis a result indicating an excess of hydrogen above that ired to form water with the oxygen, besides traces of nitrogen. Pure lose, on the other hand, is a ternary compound of carbon and the ele- ts of water, closely allied in composition to starch, if not actually eric with that substance.[1]

he properties of lignin may be conveniently studied in fine linen or on, which are almost entirely composed of the body in question, the ciated vegetable principles having been removed or destroyed by the ety of treatment to which the fibre has been subjected. Pure lignin is eless, insoluble in water and alcohol, and absolutely innutritious; it is sensibly affected by boiling water, unless it happen to have been derived a soft or imperfectly developed portion of the plant, in which case it is ntegrated and rendered pulpy. Dilute acids and alkalis exert but little on on lignin, even at a boiling temperature; strong oil of vitriol converts n the cold, into a nearly colourless, adhesive substance, which dissolves rater, and presents the character of dextrin. This curious and interest- experiment may be conveniently made by very slowly adding concen- ed sulphuric acid to half its weight of lint, or linen cut into small shreds, ng care to avoid any rise of temperature, which would be attended with rring or blackening. The mixing is completed by trituration in a mor- and the whole left to stand a few hours; after which it is rubbed up water, and warmed, and filtered from a little insoluble matter. The tion may then be neutralized with chalk, and again filtered. The gummy id retains lime, partly in the state of sulphate, and partly in combina- with a peculiar acid, composed of the elements of sulphuric or hypo- huric acid, in union with those of the lignin, to which the name sulpho- ic acid is given. If the liquid, previous to neutralization, be boiled ing three or four hours, and the water replaced as it evaporates, the trin becomes entirely changed to grape-sugar. Linen rags may, by e means, be made to furnish more than their own weight of that sub- ice.

ignin is not coloured by iodine.

DUCTS ARISING FROM THE ALTERATION OF THE PRECEDING SUBSTANCES BY CHEMICAL AGENTS.

ACTION OF NITRIC ACID.

XALIC ACID, $C_2O_3.HO+2HO$.—This important compound occurs ready ed in several plants, in combination with potassa as an acid salt, or h lime. It is now manufactured in large quantities as an article of

[1] *Dumas, Chimie appliquée aux Arts*, vi. 5.

commerce, by the action of nitric acid on sugar, starch, and dextrin. With the exception of gum and sugar of milk, which yield another product, all the substances comprehended in the saccharine and starch group furnish oxalic acid, as the chief and characteristic result of the long-continued action of moderately strong nitric acid at an elevated temperature.

One part of sugar is gently heated in a retort with 5 parts of nitric acid of sp. gr. 1·42, diluted with twice its weight of water; copious red fumes are disengaged, and the oxidation of the sugar proceeds with violence and rapidity. When the action slackens, heat may be again applied to the vessel, and the liquid concentrated, by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, re-dissolved in a small quantity of hot water, and the solution set aside to cool. The acid separates from a hot solution in colourless, transparent crystals derived from an oblique rhombic prism, which contain three equivalents of water, one of these being basic and inseparable, except by substitution; the other two may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, which may be sublimed in great measure without decomposition. The crystallized acid, on the contrary, is decomposed by a high temperature into carbonic and formic acids and carbonic oxide, without solid residue.

The crystals of oxalic acid dissolve in 8 parts of water at 60° (15°·5C), and in their own weight, or less, of hot water; they are also soluble in spirit. The aqueous solution has an intensely sour taste and most powerful acid action, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbonic oxide and carbonic acid; it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture. The binoxides of lead and manganese effect the same change, becoming reduced to protoxides, which combine with the unaltered acid.

Oxalic acid is formed from sugar by the replacement of the whole of the hydrogen by an equivalent quantity of oxygen.

$$\left.\begin{array}{ll}1 \text{ eq. sugar} & = C_{24}H_{18}O_{18} \\ 36 \text{ eq. oxygen} = & O_{36}\end{array}\right\} = \left\{\begin{array}{ll}12 \text{ eq. oxalic acid} = & C_{24}\ \ O_{36} \\ 18 \text{ eq. water} = & H_{18}O_{18}\end{array}\right.$$

$$C_{24}H_{18}O_{54} \qquad\qquad C_{24}H_{18}O_{54}$$

The most important salts of oxalic acid are the following:—

Neutral oxalate of potassa, KO,C_2O_3+HO. — This is prepared by neutralizing oxalic acid by carbonate of potassa. It crystallizes in transparent rhombic prisms, which become opaque and anhydrous by heat, and dissolve in 3 parts of water. Oxalate of potassa is often produced when a variety of organic substances are cautiously heated with excess of caustic alkali.

Binoxalate of potassa, $KO,2C_2O_3+3HO$. — Sometimes called salt of *sorrel*, from its occurrence in that plant. This, or the substance next to be mentioned, is found also in the *rumex* and *oxalis acetosella*, and in the garden rhubarb, associated with malic acid. It is easily prepared by dividing a solution of oxalic acid, in hot water, into two equal portions, neutralizing one with carbonate of potassa, and adding the other; the salt crystallizes on cooling, in colourless rhombic prisms. The crystals have a sour taste, and require 40 parts of cold, and 6 of boiling water for solution.

Quadroxalate of potassa, $KO,4C_2O_3+7HO$. — Prepared by a process similar in principle to that last described. The crystals are modified octohedrons, and are less soluble than those of the binoxalate, which the salt in other respects resembles.

Oxalate of soda, NaO,C_2O_3, has but little solubility; a binoxalate exists

F AMMONIA, NH_4O,C_2O_3+HO. — This beautiful salt is prepared
ng by carbonate of ammonia a hot solution of oxalic acid. It
n long, colourless, rhombic prisms, which effloresce in dry air
water of crystallization. They are not very soluble in cold
eely dissolve by the aid of heat. Oxalate of ammonia is of great
lytical chemistry, being employed to precipitate lime from its
hen oxalate of ammonia is heated in a retort, it is completely
yielding water, ammonia and carbonate of ammonia, cyanogen
acid gases, and a small quantity of a peculiar greyish white
The latter bears the name of *oxamide;* it is a very remarkable
rms the type of a large class of substances containing the ele-
ammoniacal salt, *minus* those of water. Oxamide is composed
.e., $NH_4O,C_2O_3—2HO$, or the elements of 1 eq. amidogen, and
c oxide. It is insoluble in water and alcohol: when boiled with
rnishes an oxalate of the base, and ammonia, which is expelled;
ted with an acid, it produces an ammoniacal salt. When treated
acid it likewise reproduces oxalic acid, pure nitrogen being
$NO_2+NO_3=C_2O_3,HO+HO+2N$. Oxamide is the representa-
ably large class of bodies having very analogous chemical rela-
parently a common constitution. Oxamide is obtained purer
ındantly from oxalic ether; its preparation will be found des-
the head of that substance. Oxalate of ammonia, when dis-
nhydrous phosphoric acid, loses four equivalents of water and
lerable quantity of cyanogen, $NH_4O,C_2O_3—4HO=C_2N$. There
other compounds simultaneously produced.
late of ammonia is still less soluble than the oxalate. When
ated in an oil-bath to 450° (232°·2C), among other products an
he *oxamic* is generated, containing $C_4H_2NO_5,HO$, i. e., NH_4O,
—2HO, and may be viewed as a compound of oxalic acid with
forms soluble compounds with lime and baryta. When heated
; yields ammonia and oxalate; hot oil of vitriol resolves it into
e and carbonic acid; and water converts it, at a boiling tem-
binoxalate of ammonia. Oxamic acid too, is interesting as the
large class of similarly constructed compounds.
F LIME, CaO,C_2O_3+2HO.—This compound is formed whenever
an oxalate is added to a soluble salt of lime; it falls as a white
n acquires density by boiling, and is but little soluble in hydro-
ntirely insoluble in acetic acid. Nitric acid dissolves it easily.
t 212° (100°C) it retains an equivalent of water, which may be
a rather higher temperature. Exposed to a red-heat in a close
nverted into carbonate of lime, with escape of carbonic oxide.
s of *baryta, zinc, manganese, protoxide of iron, copper, nickel,* and
arly insoluble in water; that of *magnesia* is sparingly soluble,
e *sesquioxide of iron* freely soluble. The double *oxalate of chro-*
assa, made by dissolving in hot water 1 part bichromate of po-
binoxalate of potassa, and 2 parts crystallized oxalic acid, is
ost beautiful salts known. The crystals appear black by re-
from the intensity of their colour, which is pure deep blue;
soluble. The salt contains $3(KO,C_2O_3)+Cr_2O_3,3C_2O_3+HO$. A
compound containing sesquioxide of iron has been formed; it
eely, and has a beautiful green colour.
ACID, $C_6H_4O_7,HO$. — This substance was once thought to be
malic acid, which is not the case; it is formed by the action
c acid on sugar, and is often produced in the preparation of
ing, from its superior solubility, found in the mother-liquor
e oxalic acid has crystallized. It may be made by heating to-

commerce, by the action of nitric acid on sugar, st ... ater. When the re-
the exception of gum and sugar of milk, whic' ... neutralised with chalk,
the substances comprehended in the sacch ... The insoluble saccharate
oxalic acid, as the chief and characterist ... ...tted hydrogen. The acid
action of moderately strong nitric acid at ... ...sistence in long colourless
One part of sugar is gently heated in ... ...e salts with lime and baryta.
of sp. gr. 1·42, diluted with twice its ... ...o precipitate, but, on the addi-
are disengaged, and the oxidation of ... ...ce separates, which is reduced,
rapidity. When the action slacke ... silver, the vessel being lined with
vessel, and the liquid concentrate ... ...tal. Nitric acid converts the sac-
acid, until it deposits crystals o ...
in a small quantity of hot wate ... ...arch is mixed with nitric acid of spe-
acid separates from a hot solu ... ...t disengagement of gas into a trans-
from an oblique rhombic pri ... ...s put into water, yields a white, curdy,
one of these being basic an ... ...w body *xyloidin*. When dry, it is white
two may be expelled by s ... ...ing water, but freely dissolved by dilute
a soft white powder, w ... ...is oxalic acid when boiled. Other sub-
decomposition. The cr ... ...ces also yield xyloidin; paper dipped into
high temperature into ... ...r plunged into water, and afterwards dried,
solid residue. ... ...l: it assumes the appearance of parchment,
The crystals of ox ... ...degree of combustibility.
in their own weig' ... ...ous matter, as cotton-wool, be steeped for a
The aqueous solut ... nitric acid of sp. gr. 1·5 and concentrated sul-
action, and is hi ... ...ughly washed and dried by very gentle heat, it
Oxalic acid is ... ...ed in weight about 70 per cent., and to have be-
oxide and carb ... ...explosive, taking fire at a temperature not much
acid, whence a ... ...d burning without smoke or residue. This is
binoxides of ... ...f Professor Schoenbein. It differs from xyloidin
to protoxides ... ...e of combustion, and in resisting the action of cer-
Oxalic aci ... ...taining a little alcohol, which dissolve xyloidin with
hydrogen b ... ...this description the name *collodion* has been given:

1 ... ...roxylin appear to the substitution-compounds, in
36 ... ...yponitric acid replace respectively 3 and 5 equiva-
... ...ose of water in starch and lignin. The analytical
... ...orm, but the formulæ which best agree with them
... and pyroxylin $C_{24}H_{15}N_5O_{40}$.[1]

The ... ...and is produced by the action of nitric acid upon
NEUT ... This substance may be crystallized from spirit, and
neutral ... ...t may be viewed as mannite, in which three equiva-
rent ... ...replaced by hyponitric acid.
solve ... 2HO. — Sugar of milk and gum, heated with nitric
variet ... furnish, in addition to a small quantity of oxalic acid,
alkali
B
sorre
men
phu
luti
wit
co
re

si
dr
ol

[1] ... the mixture of nitric and sulphuric acids, or by the action of ... parts of nitrate of potassa and three parts of concentrated sul- ... ...osition as given in the text, but is wholly insoluble in ether ... ...alcohol. When, however, the cotton-wool is steeped in the mixture ... at the temperature produced by their mixture, the resulting ... ether and a mixture of ether and alcohol forming a transparent ... passed through this solution renders it quite fluid. The ammo- ... a large quantity of water yields a light white precipitate, ...ate of ammonia remains in solution. The composition of the ... between xyloidin and pyroxylin. $C_{24}H_{17}N_4O_{36}$, four equivalents of ... four of hyponitric acid or four equivalents of the elements of ... It may be dried without alteration at the boiling temperature ... with a slight residue of carbon.
... and nitric acid forms from gum, glucose, and dextrine, explosive ... not yet been fully examined. (Bechamp, Ann. Ch. et Phys. 3d.

...e called *mucic* acid. It may be easily pre-
...or retort 1 part of milk-sugar, or gum,
..., the mucic acid is afterwards collected
... has a slightly sour taste, reddens vege-
...a bases. It requires for solution 66 parts
... dissolves it with red colour. Mucic acid is
..., among other products, a volatile acid, the
...n water, and crystallizes in a form resembling
...mucic acid is monobasic; it contains $C_{10}H_3O_5,HO$.
...$_3$,2HO, is formed by the action of nitric acid on the
... of cork, and also on certain fatty bodies; it much
..., but is more soluble in water. It is a bibasic acid.
...ion VII., Oils and Fats.

...odies are closely allied in composition to oxalic acid:—

...D, C_4O_3,HO.—This substance occurs, in combination with ...ery rare mineral called *mellite* or *honey-stone*, found in deposits ... coal, or *lignite*. It is soluble in water and alcohol, and is crys- ...forming colourless needles. It combines with bases: the melli- ...ne alkalis are soluble and crystallizable; those of the earths and ...pper are mostly insoluble.

...te of ammonia yields by distillation two curious compounds, *para-* ...*euchronic acid*. The former is a white, amorphous, insoluble sub- ...ntaining C_8HNO_4, (i. e., bimellitate of ammonia—4 eq. of water), ...ertible by boiling with water into bimellitate of ammonia. The ...ms colourless, sparingly soluble crystals containing in the anhy- ...te $C_{12}NO_6,2HO$. In contact with metallic zinc and deoxidizing ... general, euchronic acid yields a deep blue insoluble substance called

...ONIC and CROCONIC ACIDS.—When potassium is heated in a stream ...rbonic oxide gas, the latter is absorbed in large quantity, and a ...ous substance generated, which, when put into water, evolves in- ... gas, and produces a deep red solution containing the potassa-salt ...liar acid; the *rhodizonic;* by adding alcohol to the liquid, the rho- ...f potassa is precipitated. This and the lead-salt are the only two ...s which have been fully examined; the acid itself cannot be iso- ...hodizonate of potassa is composed of $C_7O_7 3KO$; hence the acid ...ear to be tribasic.

...olution of rhodizonate of potassa is boiled, it becomes orange-yel- ... decomposition of the acid, and is then found to contain oxalate of ...ree potassa, and a salt of an acid to which the term *croconic* is ... This acid can be isolated; it is yellow, easily crystallizable, and ...oth in water and alcohol. Crystallized croconic acid contains

THE FERMENTATION OF SUGAR, AND ITS PRODUCTS.

...m fermentation is applied in chemistry to a peculiar metamorpho- ...omplex organic substance, by a transportation of its elements under ...y of an external disturbing force, different from ordinary chemical ..., and more resembling those obscure phenomena of contact already ...o which the expression *katalysis* is sometimes applied. The expla ...ich Liebig has suggested of the cause and nature of the fermen- ...nge is a very happy one, although of necessity only hypothetical ...g been known that one of the most indispensable conditions of that ... the presence in the fermenting liquid of certain azotized substan- ...l *ferments*, whose decomposition proceeds simultaneously with that ...y *undergoing metamorphosis*. They all belong to the class of al-

buminous principles, bodies which in a moist condition putrefy and de pose spontaneously. It is imagined that when these substances, in th of undergoing change, are brought into contact with neutral ternary pounds of small stability, as sugar, the molecular disturbance of the already in a state of decomposition, may be, as it were, propagated other, and bring about destruction of the equilibrium of forces to wi owes its being. The complex body under these circumstances, bre into simpler products, which possess greater permanence. Whatev be the ultimate fate of this ingenious hypothesis, it is certain that posing azotized bodies not only do possess very energetic and extrao powers of exciting fermentation, but that the *kind* of fermentation se in a great degree, dependent on the phase or stage of decomposition ferment.

ALCOHOL; VINOUS FERMENTATION.—A solution of pure sugar, in or close vessel, may be preserved unaltered for any length of time; putrescible azotized matters be present, in the proper state of de sugar is converted into alcohol, with escape of carbonic acid. Putri white of egg, or flour-paste, will effect this; by far the most potent ferment is, however, to be found in the insoluble, yellowish, viscid deposited from beer in the act of fermentation, called *yeast*. If th be dissolved in a large quantity of water, a due proportion of acti added, and the whole maintained at a temperature of 70° (21·1C (26°·6C), the change will go on with great rapidity. The gas dis will be found to be nearly pure carbonic acid; it is easily collected amined, as the fermentation, once commenced, proceeds perfectly w close vessel, as a large bottle or flask, fitted with a cork and cor tube. When the effervescence is at an end, and the liquid has becom it will yield alcohol by distillation. Such is the origin of this import pound; it is a product of the metamorphosis of sugar, under the of a ferment.

The composition of alcohol is expressed by the formula $C_4H_6O_2$: duced by the breaking up of an equivalent of grape-sugar, $C_{24}H_2$ 4 eq. of alcohol, 8 of carbonic acid, and 4 of water. It is grape-su which yields alcohol, the ferment in the experiment above related verting the cane-sugar into that substance. Milk-sugar may someti rently be made to ferment, but a change into grape-sugar always r cedes the production of alcohol.

The spirit first obtained by distilling a fermented saccharine liqu weak, being diluted with a large quantity of water. By a secon tion, in which the first portions of the distilled liquid are collecte may be greatly strengthened; the whole of the water cannot, ho thus removed. The strongest rectified spirit of wine of comme density of about 0·835, and yet contains 13 or 14 per cent. of wat or *absolute* alcohol may be obtained from this by re-distilling it wit weight of fresh quick-lime. The lime is reduced to coarse powde into a retort; the alcohol is added, and the whole mixed by agitat neck of the retort is securely stopped with a cork, and the mixtu several days. The alcohol is distilled off by the heat of a water-b

Pure alcohol is a colourless, limpid liquid, of pungent and agree and odour; its specific gravity at 60° (15°·5C) is 0·7938, and t vapour 1·613. It is very inflammable, burning with a pale bluish from smoke, and has never been frozen. Alcohol boils at 173° (78° in the anhydrous condition; in a diluted state the boiling-point being progressively raised by each addition of water. In the act a *contraction* of volume occurs, and the temperature of the mi many degrees, this takes place not only with pure alcohol, but wi

miscible with water in all proportions, and, indeed, has a great ɪr the latter, absorbing its vapour from the air, and abstracting from membranes and other similar substances immersed in it. powers of alcohol are very extensive; it dissolves a great num- compounds, and likewise a considerable proportion of potassa. ɔf these substances it forms definite compounds. The substance duced by potassa, contains C_4H_5O,KO; it may be likewise formed :h potassium upon anhydrous alcohol, when hydrogen is evolved. olves, moreover, many organic substances, as the vegeto-alkalis, tial oils, and various other bodies; hence its great use in chemi- .tions and in several of the arts.

ʒth of commercial spirit is inferred from its density, when free ɪnd other substances added subsequent to distillation; a table ɪe proportions of real alcohol and water in spirits of different l be found at the end of the volume. The excise *proof spirit* has 0·9198 at 60° (15°·5C), and contains 49½ per cent. by weight of

r, &c., owe their intoxicating properties to the alcohol they con- antity of which varies very much. Port and sherry, and some wines, contain, according to Mr. Brande, from 19 to 25 per cent. while in the lighter wines of France and Germany it sometimes as 12 per cent. Strong ale contains about 10 per cent., ordinary ɔrandy, gin, whisky, 40 to 50 per cent., or occasionally more. owe their characteristic flavours to certain essential oils, present l quantity, either generated in the act of fermentation or pur- l.

; wine, the expressed juice of the grape is simply set aside in where it undergoes spontaneously the necessary change. The bumin of the juice absorbs oxygen from the air, runs into decom- l in that state becomes a ferment to the sugar, which is gradu- ed into alcohol. If the sugar be in excess, and the azotized mat- , the resulting wine remains sweet; but if, on the other hand, on of sugar be small, and that of albumin large, a *dry* wine is When the fermentation stops, and the liquor becomes clear, it is om the lees, and transferred to casks, to ripen and improve.

r of red wine is derived from the skins of the grapes, which in re left in the fermenting liquid. Effervescent wines, as cham- ɔottled before the fermentation is complete; the carbonic acid is ɪnder pressure, and retained in solution in the liquid. The pro- s much delicate management.

e fermentation of the grape-juice, or *must*, a crystalline, stony ed *argol*, is deposited. This consists chiefly of acid tartrate of th a little tartrate of lime and colouring matter, and is the l the tartaric acid met with in commerce. The salt in question e juice in considerable quantity; it is but sparingly soluble in till less so in dilute alcohol; hence, as the fermentation proceeds, ntity of spirit increases, it is slowly deposited. The acid of the removed as the sugar disappears. It is this circumstance which ɔe-juice alone fit for making good wine: when that of gooseber- ɪnts is employed as a substitute, the malic and citric acids which contain cannot be thus withdrawn. There is, then, no other t to add sugar in sufficient quantity to mask and conceal the ity of the liquor. Such wines are necessarily acescent, prone to mentation, and, to many persons, at least, very unwholesome.

well-known liquor, of great antiquity, prepared from germinated *ɪlly barley, and is* used in countries where the vine does not

and the mixture left to stand during the space of two hours or m
easily soluble diastase has thus an opportunity of acting upon th
starch of the grain, and, changing it into dextrin and sugar.
liquor, or *wort*, strained from the exhausted malt, is then pumpe
per boiler, and boiled with the requisite quantity of hops, for com
a pleasant bitter flavour, and conferring on the beer the proper
ing without injury. The flowers of the hop contain a bitter, res
ciple, called *lupulin*, and an essential oil, both of which are usef

When the wort has been sufficiently boiled, it is drawn from
and cooled, as rapidly as possible, to near the ordinary tempera
air, in order to avoid an irregular acid fermentation, to which it
erwise be liable. It is then transferred to the fermenting vessel
large breweries are of great capacity, and mixed with a quanti
the product of a preceding operation, by which the change is
duced. This is the most critical part of the whole operation,
which the skill and judgment of the brewer are most called into
process is in some measure under control by attention to the tem
the liquid, and the extent to which the change has been carri
known by the diminished density, or *attenuation*, of the wort. Th
tion is never suffered to run its full course, but is always stoppe
ticular point, by separating the yeast, and drawing off the beer
A slow and almost insensible fermentation succeeds, which in t
the beer stronger and less sweet than when new, and charges it w
acid.

Highly coloured beer is made by adding to the malt a small
strongly dried or charred malt, the sugar of which has been chan
mel; porter and stout are so prepared.

The yeast of beer is a very remarkable substance, and has ex
attention. To the naked eye it is a greyish-yellow soft solid, near
in water, and dries up to a pale brownish mass, which readily pu
moistened, and becomes offensive. Under the microscope it exh
of organized appearance, being made up of little transparent glob
sometimes cohere in clusters or strings, like some of the lowest

far as possible by large and repeated doses of yeast. Alcohol ıred in many cases from potatoes; the potatoes are ground to with hot water and a little malt, to furnish diastase, made to l then the fluid portion distilled. The potato-spirit is contami-ery offensive volatile oil, again to be mentioned; the crude pro-ırn contains a substance of a similar kind. The business of the sists in removing or modifying these volatile oils, and in replacing ers of a more agreeable character.

g bread, the vinous fermentation plays an important part; the to the dough converts the small portion of sugar the meal natu-as into alcohol and carbonic acid. The gas thus disengaged ugh and adhesive materials into bubbles, which are still farther y the heat of the oven, which at the same time dissipates the ıce the light and spongy texture of all good bread. Sometimes f ammonia is employed with the same view, being completely y the high temperature of the oven. Bread is now sometimes ing a little hydrochloric and carbonate of soda in the dough; if ortions be taken, and the whole throughly mixed, the operation be very successful. The use of *leaven* is one of great antiquity; ly dough in a state of incipient putrefaction. When mixed with tity of fresh dough, it excites in the latter the alcoholic fermenta-ame manner as yeast, but less perfectly; it is apt to communicate ole sour taste and odour.

ID; LACTIC ACID FERMENTATION; BUTYRIC ACID FERMENTATION. lbuminous substances, which in an advanced state of putrefactive as alcohol-ferments, often possess, at certain periods of decay, the inducing an acid fermentation in sugar, the consequence of which rsion of that substance into *lactic acid.* Thus, the azotized matter en suffered to putrefy in water for a few days, acquires the power g the sugar which accompanies it, while in a more advanced state sition it converts, under similar circumstances, the sugar into e glutin of grain behaves in the same manner: wheat flour, made with water, and left four or five days in a warm situation, be-e lactic acid ferment; if left a day or two longer, it changes its nd then acts like common yeast. Moist animal membranes, in a aying condition, often act energetically in developing lactic acid. ar, probably by previously becoming grape-sugar, and the sugar h yield lactic acid, the latter, however, most readily, the grape-g a strong tendency towards the alcoholic change. A good method g lactic acid is the following. An additional quantity of milk-solved in ordinary milk, which is then set aside in a warm place, mes sour and coagulated. The casein of the milk absorbs oxygen ir, runs into putrefaction, and acidifies a portion of the sugar. acid formed, after a time coagulates and renders insoluble the the production of that acid ceases. By carefully neutralizing, ie free acid by carbonate of soda, the casein becomes soluble, ng its activity, changes a fresh quantity of sugar into lactic acid, be also neutralized, and by a sufficient number of repetitions of all the sugar of milk present may, in time, be acidified. When en place, the liquid is boiled, filtered, and evaporated to dryness bath. The residue is treated with hot alcohol, which dissolves out of soda. The alcoholic solution may then be decomposed by the dition of sulphuric acid, which precipitates sulphate of soda, inso-rit. The free acid may, if needful, be neutralized with lime, and g salt purified by re-crystallization and the use of animal char-*which it may be decomposed* by oxalic acid

The following process will be found more economical on a large scale. A mixture is made of two gallons of milk, which may be stale or skimmed milk, six pounds of raw sugar, twelve pints of water, eight ounces of putrid cheese, and four pounds of chalk, which should be mixed up to a cream-like consistence with some of the liquid. This mixture is exposed in a loosely covered jar to a temperature of about 86° (30°C), with occasional stirring. At the end of two or three weeks it will be found converted into a semi-solid mass or pudding of lactate of lime, which may be drained, pressed, and purified by re-crystallization from water.

The lactate of lime may be decomposed by the necessary quantity of pure oxalic acid, the filtered liquor neutralized with carbonate of zinc, and, after a second filtration, evaporated until the zinc-salt crystallizes out on cooling. The latter may, lastly, be re-dissolved in water, and decomposed by sulphuretted hydrogen, in order to obtain the free acid.

If in the first part of the process the solid lactate of lime be not removed at the proper period from the fermenting liquid, it will gradually re-dissolve and disappear. On examination the liquid will then be found to consist chiefly of a solution of *butyrate of lime*.

This second stage of the process, to which the name of *butyric acid fermentation* has been given, is attended with an evolution of hydrogen and carbonic acid. It will be mentioned more in detail in the Section on Oils and Fats.

Lactic acid may be extracted from a great variety of liquids containing decomposing organic matter, as *sauerkraut*, a preparation of white cabbage, the sour liquor of the starch-maker, &c. It has been supposed to exist in the blood, urine, and other animal fluids; recent researches have, however, failed to detect it in either blood or urine, although it has been shown by Liebig to exist in considerable quantity in the juice of flesh or muscle.

Lactic acid has been lately produced artificially in a most remarkable manner by the action of nitrous acid upon *alanine*. (See the Section on Organic Bases.)

Solution of lactic acid may be concentrated in the vacuum of the air-pump, over a surface of oil of vitriol, until it acquires the aspect of a colourless, syrupy liquid, of sp. gr. 1·215. It has an intensely sour taste and acid reaction; it is hygroscopic, and very soluble in water, alcohol, and ether. It forms soluble salts with all the metallic oxides. The syrupy acid contains $C_6H_5O_5+HO$, or $C_{12}H_{10}O_{10}+2HO$, the water being basic, and susceptible of replacement by a metallic oxide.

When syrupy lactic acid is heated in a retort to 266° (130°C), water containing a little actic acid distils over, and the residue on cooling forms a yellowish solid fusible mass, very bitter, and nearly insoluble in water. This is anhydrous lactic acid, $C_6H_5O_5$. Long-continued boiling with water converts it into ordinary lactic acid. When this substance is farther heated it decomposes, yielding numerous products. One of these is *lactide*, formerly erroneously called anhydrous lactic acid, a volatile substance, crystallizing in brilliant colourless rhombic plates, which, when put into water, slowly dissolve, with production of common lactic acid. Lactide contains $C_6H_4O_4$; it combines with ammonia, forming *lactamide*, $C_6H_7NO_4$, a colourless, crystallizable, soluble substance, resembling in its chemical relations oxamide. Another product of the action of heat on lactic acid is *lactone*, a colourless volatile liquid, boiling at 198° (92°·2C.) Acetone is also formed, and carbonic oxide and carbonic acid are disengaged.

A salt of lactic acid, gently heated with five or six parts of oil of vitriol, yields an enormous quantity of perfectly pure carbonic oxide gas.

The most important and characteristic of the lactates are those of lime and the oxide of zinc.

ACTATE OF LIME, $CaO,C_6H_5O_5+5HO$, exists ready-formed, to a small ex-, in *Nux vomica*. When pure, it crystallizes in tufts of minute white lles grouped in concentric layers. It dissolves in 10 parts of cold, and finitely in boiling water, melting in its water of crystallization at that perature.

ACTATE OF ZINC, $ZnO,C_6H_5O_5+3HO$, is deposited from a hot solution in ll brilliant 4-sided prismatic crystals, which require for solution 58 parts old and 6 of boiling water.

ACTATE OF PROTOXIDE OF IRON, $FeO,C_6H_5O_5+3HO$, is now used in medi-. It is prepared by adding alcohol to a mixture of lactate of ammonia protochloride of iron, when the salt is precipitated in the form of small owish needles.

Then the expressed juice of the beet is exposed to a temperature of 90° ·9C) or 100° (37°·7C) for a considerable time, the sugar it contains ers a peculiar kind of fermentation, to which the term *viscous* has been lied. Gases are evolved which contain hydrogen, and when the change ears complete, and the products come to be examined, the sugar is found ave disappeared. Mere traces of alcohol are produced, but, in place of substance, a quantity of lactic acid, mannite, and a mucilaginous subce resembling gum-Arabic, and said to be identical with gum in comtion.

ure sugar can be converted into this substance; by boiling yeast or the in of wheat in water, dissolving sugar in the filtered solution, and exng it to a tolerably high temperature, the viscous fermentation is set up, a large quantity of the gummy principle generated. A little gas is at same time disengaged, which is a mixture of carbonic acid and hydrogen.

PRODUCTS OF THE ACTION OF ACIDS ON ALCOHOL.

THER; OXIDE OF ETHYL.—When equal weights of rectified spirit and oil itriol are mixed in a retort, the latter connected with a good condensing ngement, and the liquid heated to ebullition, a colourless and highly vo-e liquid, long known under the name of *ether*, or *sulphuric ether*, distils . The process must be stopped as soon as the contents of the retort ken and froth, otherwise the product will be contaminated with other tances, which then make their appearance. The ether obtained may be d with a little caustic potassa, and re-distilled by a very gentle heat.

ure ether is a colourless, transparent, fragrant liquid, very thin and mo- Its sp. gr. at 60° (15°·5C) is about 0·720; it boils at 96° (35°·5C) r the pressure of the atmosphere, and bears without freezing the se-st cold. When dropped on the hand it occasions a sharp sensation of , from its rapid volatilization. Ether is very combustible; it burns with ite flame, generating water and carbonic acid. Although the substance f is one of the lightest of liquids, its vapour is very heavy, having a ity of 2·586. Mixed with oxygen gas, and fired by the electric spark, therwise, it explodes with the utmost violence. Preserved in an imper-y-stopped vessel, ether absorbs oxygen, and becomes acid from the pro-ion of acetic acid; this attraction for oxygen is increased by elevation emperature. It is decomposed by transmission through a red-hot tube olefiant gas, light carbonetted hydrogen, and a substance yet to be de-ed, *aldehyde*.

Ether is miscible with alcohol in all proportions, but not with water; it dissolves to a small extent in that liquid, 10 parts of water taking up 1 part, or thereabouts, of ether. It may be separated from alcohol, provided the quantity of the latter be not excessive, by an addition of water, and in this manner samples of commercial ether may be conveniently examined. Ether is a solvent for oily and fatty substances generally, and phosphorus to a small extent, a few saline compounds and some organic principles, but its powers in this respect are much more limited than those of alcohol or water.

Ether was the first part of a great number of analogous substances in which the property of producing temporary insensibility to pain was recognized. In surgical operations, the use of ether is now superseded by that of chloroform.

Ether is found by analysis to contain C_4H_5O; it, therefore, differs from alcohol, $C_4H_6O_2$, by the elements of water. Alcohol is often regarded as the hydrate of ether; but as ether cannot be made to combine with water directly, and as alcohol cannot be converted into ether by the abstraction of water by the aid of substances known to possess a high affinity for that liquid, such a view was always looked upon as hypothetical. Recent experiments have, in fact, shown that a very different relation exists between alcohol and ether. We shall return to these researches, when we consider the theory of the production of ether, which will be discussed partly in connection with the history of sulphovinic acid, and partly with that of the methyl-compounds.

COMPOUND ETHERS; ETHYL-THEORY; ETHYL.—The so-called compound ethers constitute a very large and important class of substances derived from alcohol, and containing either the elements of ether, in combination with those of an oxygen-acid, inorganic or organic, or the elements of olefiant gas in union with those of a hydrogen-acid. The relations of these compounds to alcohol and the acids are most simply and clearly illustrated by comparing them with ordinary salts, in which the metal is replaced by a salt-basyle termed *ethyl*, containing C_4H_5. This substance forms haloid-salts by combining with chlorine, iodine, bromine, &c., and its oxide, identical or isomeric with common ether, with oxygen-acids, like basic metallic oxides in general. A body containing carbon and hydrogen in the proportions indicated by the formula C_4H_5, has been lately obtained by Dr. Frankland, from one of the members of this group of compounds, and described under the name of *ethyl*. It is formed by exposing iodide of ethyl in sealed tubes, to the action of metallic zinc, at a temperature of 320° (160°C).[1] In this reaction, the iodine of the iodide of ethyl C_4H_5I combines with the zinc, and ethyl is set free. On opening the sealed tubes, and allowing the gas, which is ethyl mixed with several secondary products (especially olefiant gas), to pass into a freezing mixture, the temperature of which is kept below —9° (—23°C), the ethyl condenses to a colourless mobile liquid. It is not attacked by concentrated sulphuric and nitric acids. Chlorine acts upon it under the influence of light, but not in the dark. Hitherto no compound ether has been reproduced from ethyl. The ethyl-theory, proposed by the sagacity of Liebig long before the separation of ethyl itself, will be found highly useful as an aid to the memory; it must not, however, be forgotten that the compound ethers are distinguished by important characters from real and undoubted salts.

Table of Ethyl-Compounds.

Ethyl, symbol Ae	C_4H_5
Oxide of ethyl; ether	C_4H_5O
Hydrate of the oxide; alcohol	C_4H_5O,HO

[1] See also, zinc-ethyl, page 368.

Chloride of ethyl	C_4H_5Cl
Bromide of ethyl	C_4H_5Br
Iodide of ethyl	C_4H_5I
Cyanide of ethyl	C_4H_5Cy
Nitrate of oxide of ethyl	C_4H_5O,NO_5
Nitrite of oxide of ethyl	C_4H_5O,NO_3
Oxalate of oxide of ethyl	C_4H_5O,C_2O_3
Hydride of ethyl	C_4H_5H
Zinc-ethyl	C_4H_5Zn
&c. &c.	

he ethers of many of the acids may be formed by the direct action of e latter upon alcohol at a high temperature, the elements of water being laced by those of the acid; this is chiefly conspicuous with the volatile s. A more ready general method of forming them, however, is to distil xture of alcohol, sulphuric acid, and a salt of the acid the ether of which equired. The fatty acids, which in general cannot be distilled without e or less decomposition, yield their ethers with great facility by the action ydrochloric acid gas upon an alcoholic solution of the acid.

he compound ethers are mostly volatile aromatic liquids, in a few cases tallizable solids, without action on vegetable colours, sparingly soluble ater, but dissolved in all proportions by alcohol and ether. They are acted upon in the cold by alkaline carbonates, but suffer decomposition more or less difficulty when heated with aqueous solutions of caustic li, a salt of the acid of the ether being usually generated, and alcohol ed and set free. An alcoholic solution of hydrate of potassa or soda is e active in this respect. The same kind of decomposition is often ght about by the prolonged contact of boiling water.

HLORIDE OF ETHYL; LIGHT HYDROCHLORIC ETHER; AeCl.—Rectified it of wine is saturated with dry hydrochloric acid gas, and the product illed with very gentle heat; or a mixture of 3 parts oil of vitriol and 2 lcohol is poured upon 4 parts of dry common salt in a retort, and heat lied; in either case the vapour of the hydrochloric ether should be conted through a little tepid water in a wash-bottle, and then conveyed into all receiver surrounded by ice and salt. It is purified from adhering er by contact with a few fragments of fused chloride of calcium. Hyhloric ether is a thin, colourless, and excessively volatile liquid, of a etrating, aromatic, and somewhat alliaceous odour. At the freezing point ater, its sp. gr. is 0·921, and it boils at 50° (12°·5C); it is soluble in 10 ts of water, is not decomposed by solution of nitrate of silver, but is kly resolved into chloride of potassium and alcohol by a hot solution of stic potassa.

ROMIDE OF ETHYL; HYDROBROMIC ETHER; AeBr.—This is prepared by illing a mixture of 8 parts bromine, 1 part phosphorus, and 32 parts hol. The phosphorus is converted into phosphorous acid by the oxygen he alcohol, when the ethyl combines with the bromine; 3 equivalents of hol, 3 equivalents of bromine, and 1 equivalent of phosphorus, yield 3 ivalents of bromide of ethyl, 3 equivalents of water, and 1 equivalent of phorous acid. It is a very volatile liquid, boiling at 106° (41°C), of etrating taste and smell, and superior in density to water.

ODIDE OF ETHYL; HYDRIODIC ETHER; AeI.—Obtained by gradually mix- with precaution, 1 part of phosphorus, 5 parts of alcohol, and 10 parts odine (1 eq. of phosphorus, 3 eq. of alcohol, and 3 eq. of iodine), and illing. The reaction is analagous to that described in the case of the mide. Iodide of ethyl is a colourless liquid, of penetrating and ethereal ur, *having a density of 1·92*, and boiling at 158° (70°C). It becomes red

30*

by contact with air from a commencement of decomposition. This substance has become highly important as a source of ethyl, and from its remarkable deportment with ammonia, which will be discussed in the Section on Organic Bases.

SULPHIDE OF ETHYL; AeS.—Formed by the action of chloride of ethyl upon a solution of the protosulphate of potassium. It is colourless, has a disagreeable garlic odour, and boils at 180° (82°C).

CYANIDE OF ETHYL, AeCy.—This is produced when a mixture of sulphovinate of potassa and cyanide of potassium, both in a dry state, is slowly heated. It is colourless, when perfectly pure it has a powerful, not disagreeable odour, and a sp. gr. of 0·788. It boils at 190°·4 (88°C). This substance has lately been studied by Drs. Kolbe and Frankland. They have found that cyanide of ethyl differs from the ordinary ethers in its deportment with the alkalis. Instead of yielding cyanide of potassium and alcohol, it is converted into ammonia and propionic acid, $C_6H_5O_3,HO$, a peculiar acid closely allied to acetic acid, and which will be noticed more in detail under the head of acetone. Cyanide of ethyl, in this reaction, absorbs 4 equivalents of water:—

1 eq. of cyanide of ethyl....	C_6H_5N	1 eq. of propionic acid.......	$C_6H_6O_4$
4 eq. of water.....................	$H_4\ O_4$	1 eq. of ammonia................	H_3N
	$C_6H_9NO_4$		$C_6H_9NO_4$

(See cyanide of methyl.)—When acted upon by potassium, cyanide of ethyl furnishes a gas, the nature of which is not definitely settled; the residue contains cyanide of potassium and an organic alkali *cyanethine*, which contains $C_{18}H_{15}N_3$, and is formed by the coalescence of three equivalents of the cyanide.

SULPHITE OF OXIDE OF ETHYL; SULPHUROUS ETHER; AeO,SO_2.—This substance was obtained by adding absolute alcohol in excess to subchloride of sulphur. Hydrochloric acid is evolved, and sulphur deposited, while the sulphite of ethyl distils as a limpid strongly smelling liquid, of sp. gr. 1·085, boiling at 338° (170°C), it is slowly decomposed by water.

SULPHATE OF OXIDE OF ETHYL; SULPHURIC ETHER; AeO,SO_3.—This substance has been only recently obtained. It is formed by passing the vapour of anhydrous sulphuric acid into perfectly anhydrous ether. A syrupy liquid is produced, which is shaken with 4 vols. of water and 1 vol. of ether, when two layers are formed: the lower contains sulphovinic acid, and various other compounds, while the upper layer consists of an ethereal solution of sulphate of ethyl. At a gentle heat the ether is volatilized, and the sulphate of ethyl remains as a colourless liquid. It cannot be distilled without decomposition.

PHOSPHATE OF OXIDE OF ETHYL; PHOSPHORIC ETHER.—See phosphovinic acid.

NITRATE OF OXIDE OF ETHYL; NITRIC ETHER; AeO,NO_5.—The nitrate likewise has only recently been obtained; it is prepared by cautiously distilling a mixture of equal weights of alcohol and moderately strong nitric acid, to which a small quantity of nitrate of urea has been added. The action of nitric acid upon alcohol is peculiar; the facility with which that acid is deoxidized by combustible bodies, leads, under ordinary circumstances, to the production of nitrous acid on the one hand, and an oxidized product of alcohol on the other, a *nitrite* of the oxide of ethyl being generated instead of a nitrate. M. Millon has shown that the addition of urea, from reasons to be explained when this compound will be described, entirely prevents the *formation* of that substance, and at the same time preserves the alcohol from *oxidation* by undergoing that change in its place, the sole liquid product

sing the new ether. The experiment is most safely conducted on a small scale, and the distillation must be stopped when seven-eighths of the whole have passed over; a little water added to the distilled product separates the nitric ether. Nitric ether has a density of 1·112; it is insoluble in water, has an agreeable sweet taste and odour; and is not decomposed by an aqueous solution of caustic potassa, although that substance dissolved in alcohol attacks it even in the cold, with production of nitrate of potassa. Its vapour is apt to explode when strongly heated.

NITRITE OF OXIDE OF ETHYL; NITROUS ETHER; AeO,NO_3.—Pure nitrous ether can only be obtained by the direct action of the acid itself upon alcohol. 1 part of potato-starch, and 10 parts of nitric acid, are gently heated in a capacious retort or flask, and the vapour of nitrous acid thereby evolved conducted into alcohol mixed with half its weight of water, contained in a two-necked bottle, which is to be plunged into cold water, and connected with a good condensing arrangement. All elevation of temperature must be carefully avoided. The product of this operation is a pale yellow volatile liquid, possessing an exceedingly agreeable odour of apples; it boils at 62° (16°·6C), and has a density of 0·947. It is decomposed by potassa, without darkening, into the nitrite of the base, and alcohol.

Nitrous ether, but contaminated with aldehyde, may be prepared by the following simple method:—Into a tall cylindrical bottle or jar are to be introduced successively 9 parts of alcohol of sp. gr. 0·830, 4 parts of water, and 8 parts of strong fuming nitric acid; the two latter are added by means of a long funnel with very narrow orifice, reaching to the bottom of the bottle, so that the contents may form three distinct strata, which slowly mix from the solution of the liquids in each other. The bottle is then loosely stopped, and left two or three days in a cool place, after which it is found to contain two layers of liquids, of which the uppermost is the ether. It is purified by rectification. A somewhat similar product may be obtained by carefully distilling a mixture of 3 parts rectified spirit and 2 of nitric acid of 1·28 sp. gr.; the fire must be withdrawn as soon as the liquid boils.

The *sweet spirits of nitre* of pharmacy, prepared by distilling three pounds of alcohol with four ounces of nitric acid, is a solution of nitrous ether, aldehyde, and perhaps other substances, in spirit of wine.

CARBONATE OF OXIDE OF ETHYL; CARBONIC ETHER; AeO,CO_2.—Fragments of potassium or sodium are dropped into oxalic ether as long as gas is disengaged; the brown pasty product is then mixed with water and distilled. The carbonic ether is found floating upon the surface of the water of the receiver as a colourless, limpid liquid of aromatic odour and burning taste. It boils at 259° (126°C), and is decomposed by an alcoholic solution of potassa into carbonate of that base and alcohol. The reaction which gives rise to this substance is unexplained.

SILICIC AND BORACIC ETHERS.—A number of these compounds appear to exist, containing different proportions of the acids. *Silicic ether*, containing $3AeO,SiO_3$, was obtained by M. Ebelmen by the action of anhydrous alcohol upon chloride of silicium. It is a colourless, limpid, aromatic liquid, of sp. gr. 0·933, boiling at 329° (165°C), and decomposed by water with production of silicic acid and alcohol. In contact with moist air it is gradually resolved into translucent hydrate of silica, which becomes in the end hard enough to scratch glass. By substituting ordinary spirit for absolute alcohol, other compounds containing a larger portion of silicic acid are obtained.

Boracic ether was procured by a similar process, substituting the chloride of boron for chloride of silicium. It formed a thin, limpid liquid of agreeable odour, having the sp. gr. of 0·885, and boiling at 246° (118°C). It is decomposed by water. Its alcoholic solution burns with a fine green flame, throwing off a thick smoke of boracic acid. It contains $3AeO,BoO_3$. A second

boracic ether in the form of a solid glassy fusible substance, containing $AeO,2BoO_3$, was formed by the action of fused boracic acid upon absolute alcohol. It is volatile in the vapour of alcohol only, and is decomposed by water.

Of the ethers of the organic acids, the following are the most important:—

OXALATE OF THE OXIDE OF ETHYL; OXALIC ETHER; AeO,C_2O_3.—This compound is most easily obtained by distilling together 4 parts binoxalate of potassa, 5 parts oil of vitriol, and 4 parts strong alcohol. The distillation may be pushed nearly to dryness, and the receiver kept warm to dissipate any ordinary ether that may be formed. The product is mixed with water, by which the oxalic ether is separated from the undecomposed spirit; it is repeatedly washed to remove adhering acid, and re-distilled in a small retort, the first portions being received apart and rejected. Another very simple process consists in digesting equal parts of alcohol and dehydrated oxalic acid, in a flask furnished with a long glass tube, in which the volatilized spirit may condense. After 6 or 8 hours' digestion, the mixture generally contains only traces of oxalic acid which is not etherified.

Pure oxalic ether is a colourless, oily liquid, of pleasant aromatic odour, and 1·09 sp. gr. It boils at 363° (183°·8C) is but little soluble in water, and is readily decomposed by caustic alkalis into an oxalate and alcohol. With solution of ammonia in excess, it yields *oxamide* and alcohol. $C_4H_5O,C_2O_3+NH_3=C_2O_2,NH_2+C_4H_5O,HO$. This is the best process for preparing oxamide, which is obtained perfectly white and pure. (See page 843.) When dry gaseous ammonia is conducted into a vessel containing oxalic ether, the gas is rapidly absorbed, and a white solid substance produced, which is soluble in hot alcohol, and separates, on cooling, in colourless, transparent, scaly crystals. They dissolve in water, and are both fusible and volatile. The name *oxamethane* is given to this body; it consists of $C_8H_7NO_6=C_4H_5O$, $C_4H_2NO_5$, i. e., the ether of oxamic acid (see page 843). The same substance is formed when ammonia in small quantity is added to a solution of oxalic ether in alcohol.

When oxalic ether is treated with dry chlorine in excess in the sunshine, a white, colourless, crystalline, fusible body is produced, insoluble in water and instantly decomposed by alcohol. It contains $C_6Cl_5O_4$, or oxalic ether in which the whole of the hydrogen is replaced by chlorine.

ACETATE OF OXIDE OF ETHYL; ACETIC ETHER; $AeO,C_4H_3O_3$.—Acetic ether is conveniently made by heating together in a retort 3 parts of acetate of potassa, 3 parts of strong alcohol, and 2 of oil of vitriol. The distilled product is mixed with water, to separate the alcohol, digested first with a little chalk, and afterwards with fused chloride of calcium, and, lastly, rectified. The pure ether is an exceedingly fragrant, limpid liquid; it has a density of 0·890, and boils at 165° (73°·8C). Alkalis decompose it in the usual manner. When treated with ammonia, it yields *acetamide*, a crystalline substance soluble in water and alcohol, which contains $C_4H_5NO_2=C_4H_3O_2,NH_2$, i. e., acetate of ammonia—2 equivalents of water. Its formation is analogous to that of oxamide. Alkalis and acids reconvert it into ammonia and acetic acid. When treated with nitrous acid, it yields acetic acid, water and nitrogen gas, $C_4H_5NO_2+NO_3=C_4H_3O_3,HO+HO+2N$.

FORMATE OF THE OXIDE OF ETHYL; FORMIC ETHER; AeO,C_2HO_3.—A mixture of 7 parts of dry formate of soda, 10 of oil of vitriol, and 6 of strong alcohol, is to be subjected to distillation. The formic ether, separated by the addition of water to the distilled product, is agitated with a little magnesia, and left several days in contact with chloride of calcium. Formic ether is colourless, has an aromatic smell, and density of 0·915, and boils at 133° (56°C). Water dissolves this substance to a small extent.

The ethers of many of the vegetable acids have been obtained and described.

The ethers of cyanic and cyanuric acids have been formed and studied. The description of these remarkable substances and of their important products of decomposition is postponed until the history of the acids themselves has been given.

ETHERS OF THE FATTY ACIDS. — Normal *stearic ether* has not yet been obtained. By passing hydrochloric acid gas into an alcoholic solution of stearic acid, Redtenbacher succeeded in obtaining the compound $AeO,HO,C_{68}H_{66}O_5$. It resembled white wax, was inodorous and tasteless, melted at 86° (30°C), and could not be distilled without decomposition. It was readily decomposed by boiling with caustic alkalis. *Margaric ether* is prepared by a similar mode of proceeding. When purified from excess of acid by agitation with successive small quantities of weak spirit, and afterwards made to crystallize slowly from the same menstruum, it forms regular, brilliant, colourless crystals, fusible at 70° (21°·1C), and distilling without decomposition; when less pure it is in great part destroyed by this latter process. Margaric ether contains $AeO,C_{34}A_{33}O_3$. An *oleic ether*, and corresponding compounds of several other less important fatty acids, have been formed and described. They greatly resemble each other in characters.

BUTYRIC AND VALERIANIC ETHERS, $AeO,C_8H_7O_3$, and $AeO,C_{10}H_9O_3$. — The ether-compounds of these acids are easily obtained by the preceding process. They are fragrant volatile liquids, having an odour resembling that of the kind of the pine-apple. They are used for flavouring brandy. They are lighter than water, boil at a high temperature, and possess the constitution and general character of the class of bodies to which they belong.

ŒNANTHIC ETHER. — The aroma possessed by certain wines appears due to the presence of the ether of a peculiar acid called *œnanthic*, and which is probably generated during fermentation. When such wines are distilled on the large scale, an oily liquid passes over towards the close of the operation, which consists, in great measure, of the crude ether; it may be purified by agitation with solution of carbonate of potassa, freed from water by a few fragments of chloride of calcium, and re-distilled. Œnanthic ether is a thin, colourless liquid, having a powerful and almost intoxicating vinous odour; it has a density of 0·862, boils at 482° (250°C), and is but sparingly soluble in water, although, like the compound ethers in general, it dissolves with facility in alcohol. It contains $C_{22}H_{12}O_4$, or $AeO,C_{18}H_{17}O_3$.

A hot solution of caustic potassa instantly decomposes œnanthic ether; alcohol distils over, and œnanthate of potassa remains in the retort; the latter is readily decomposed by warm dilute sulphuric acid, with liberation of œnanthic acid. Purified by repeated washing with hot water, œnanthic acid presents the appearance of a colourless, inodorous oil, which at 77° (25°C) becomes a soft solid, like butter. It reddens litmus paper, and dissolves easily in solutions of the alkaline carbonates and in spirit, and very much resembles the fatty acids, to be hereafter described, the products of saponification. The acid thus obtained is a hydrate, composed of $C_{18}H_{17}O_3+HO$. An acid of exactly the same composition has been obtained from *Pelargonium roseum*, and described by the name of pelargonic acid. It is likewise produced, together with a host of similar acids, by the action of nitric acid upon oleic acid. Œnanthic ether may be reproduced by distilling a mixture of 5 parts sulphovinate of potassa, and 1 part hydrated œnanthic acid, or perhaps better, by the ordinary process for the ethers of the fatty acids.

CHLOROCARBONIC ETHER. — Although the constitution of this substance is doubtful, it may be here described. Absolute alcohol is introduced into a glass-globe containing chlorocarbonic acid (phosgene gas, p. 131); the gas is absorbed *in large quantity*, and a yellowish liquid produced, from which

water separates the chlorocarbonic ether. When freed from water by chloride of calcium, and from adhering acid by rectification from litharge, it forms a thin, colourless, neutral liquid, which burns with a green flame. Its density is 1·138; it boils at 202° (94°·5C). The vapour, mixed with a large quantity of air, has an agreeable odour, but when nearly pure is extremely suffocating. It contains $C_6H_5ClO_4 = C_4H_5O,C_2ClO_3$. The density of the vapour is 3·82.

The action of ammonia, gaseous or liquid, upon this substance, gives rise to a very curious product, called by M. Dumas *urethane*; sal-ammoniac is at the same time formed. Urethane is a white, solid, crystallizable body, fusible below 212° (100°C), and distilling unchanged, when in a dry state, about 356° (180°C); if moisture be present, it is decomposed, with evolution of ammonia. Water dissolves this substance very easily; the solution is not affected by nitrate of silver, and yields, by spontaneous evaporation, large and distinct crystals. It contains $C_6H_7NO_4$, or elements of carbonic ether and *urea*,—whence the name.

COMPOUND ACIDS CONTAINING THE ELEMENTS OF ETHER.

SULPHOVINIC ACID, $C_4H_5O,2SO_3,HO$. — Strong rectified spirit of wine is mixed with a double weight of concentrated sulphuric acid; the mixture is heated to its boiling point, and then left to cool. When cold, it is diluted with a large quantity of water, and neutralized with chalk; much sulphate of lime is produced. The latter is placed upon a cloth filter, drained, and pressed; the clear solution is evaporated to a small bulk by the heat of a water-bath, filtered from a little sulphate, and left to crystallize; the product is *sulphovinate of lime*, in beautiful colourless, transparent crystals, containing $CaO,C_4H_5O,2SO_3+2HO$. They dissolve in an equal weight of cold water, and effloresce in a dry atmosphere.

A similar salt, containing baryta, $BaO,C_4H_5O,2SO_3+2HO$, equally soluble, and still more beautiful, may be produced by substituting, in the above process, carbonate of baryta for chalk; from this substance the hydrated acid may be procured by exactly precipitating the base by dilute sulphuric acid, and evaporating the filtered solution, *in vacuo*, at the temperature of the air. It forms a sour syrupy liquid, in which sulphuric acid cannot be recognized, and is very easily decomposed by heat, and even by long exposure in the vacuum of the air-pump. All the sulphovinates are soluble; the solutions are decomposed by ebullition. The lead-salt resembles the barytic compound. That of potassa, easily made by decomposing sulphovinate of lime by carbonate of potassa, is anhydrous; it is permanent in the air, very soluble, and crystallizes well.

Sulphovinate of potassa, distilled with concentrated sulphuric acid, gives ether; with dilute sulphuric acid, alcohol: and with strong acetic acid, acetic ether. Heated with hydrate of lime or baryta, the sulphovinates yield a sulphate of the base and alcohol.

PHOSPHOVINIC ACID, $C_4H_5O,PO_5,2HO$. — This acid is bibasic. The baryta-salt is prepared by heating to 180° (82·°2C) a mixture of equal weights of strong alcohol and syrupy phosphoric acid, diluting this mixture, after the lapse of 24 hours, with water, and neutralizing by carbonate of baryta. The solution of phosphovinate, separated by filtration from the insoluble phosphate, is evaporated at a moderate temperature. The salt crystallizes in brilliant hexagonal plates, which have a pearly lustre, and are more soluble in cold than in hot water; it dissolves in 15 parts of water at 68° (20°C). The

...als contains $2BaO,C_4H_5O,PO_5+12HO$. From this substance the hydr... ...id may be obtained by precipitating the baryta by dilute sulphuric acid, ...vaporating the filtered liquid in the vacuum of the air pump... ...ourless, syrupy liquid, of intensely sour taste, which sometimes ... ...rances of crystallization. It is very soluble in water, ..., and easily decomposed by heat when in a concentrated state. The ...hovinates of lime, silver, and lead ... ...e alkalis, magnesia, and strontia are ...

...egeli has lately observed that ... alcohol, together with phosph... ...h he gives the name phosph... ...nated by phosphethylic acid. ... are more soluble than the ... and lime-salts are anhy... ...$CaO,2C_4H_5O.PO_5$.

...e former of these salts when heated ... 874° ... 180° and ... ...sic phosphoric ether ... ...ation is represented by the equation ... $PbO.C_4H_5O.PO_5$.

...KALOVINIC ACID ...

...s alcohol and enough ... ...ralize one-half of the ... new acid ... ...hol, but easily ... exceedingly ... ...tion of the preceding ... ...y soluble salt. ... ...e type ...

[illegible]

[illegible]

A solution of ...

which the liquid is subjected. The cause of the decomposition is to be traced to the instability of the compound itself, and to the basic power of water, and the attraction of sulphuric acid for the latter, in virtue of which it determines the production of that substance, and liberates the elements of the ether.

When the sulphovinic acid is so far diluted as to boil at 260° (126°·6C) or below, or when a temperature not exceeding this is applied to a stronger solution by the aid of a liquid bath, the compound acid is resolved into sulphuric acid, which remains behind in the retort or distillatory vessel, while alcohol, and mere traces of ether, are volatilized.

An acid whose boiling-point lies between 260° and 310° (126·6 and 154°·5C) is decomposed by ebullition into hydrated sulphuric acid and ether, which is accompanied by small quantities of alcohol.

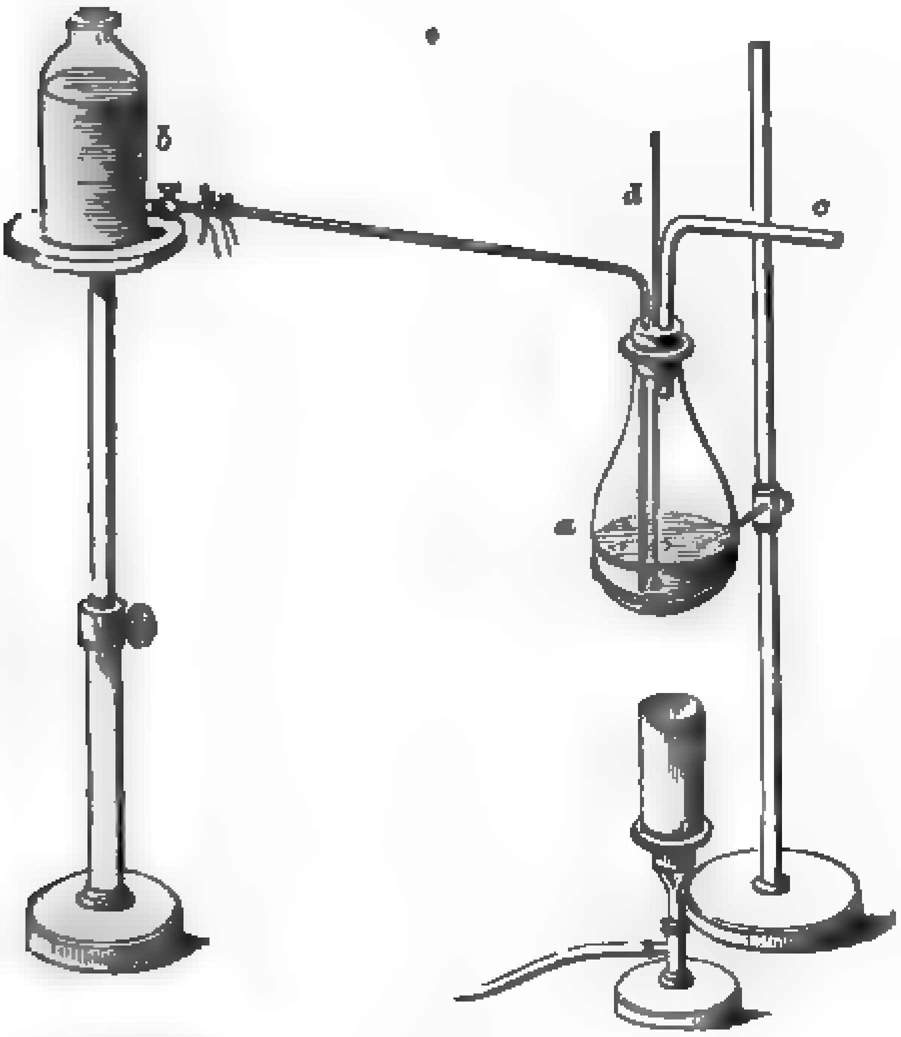
Lastly, when, by the addition of a large quantity of oil of vitriol, the boiling-point of the mixture is made to rise to 320° (160°C) and above, the production of ether diminishes, and other substances begin to make their appearance, of which the most remarkable is olefiant gas. The mixture in the retort blackens, sulphurous acid and carbonic acid are disengaged, a yellow, oily aromatic liquid passes over, and a coaly residue is left, which contains sulphur. The chief and characteristic product is the olefiant gas; the others may be considered the result of secondary actions. The three modes of decomposition may be thus contrasted:—

$$\begin{array}{lll}
\text{Below } 260^\circ\text{—}C_4H_5O,2SO_3,HO+2HO & = C_4H_5O,HO & +2(SO_3,HO) \\
260^\circ\text{—}310^\circ\text{—}C_4H_5O,2SO_3,HO+\ HO & = C_4H_5O & +2(SO_3,HO) \\
\text{Above } 320^\circ\text{—}C_4H_5O,2SO_3,HO & = C_4H_4 & +2(SO_3,HO)
\end{array}$$

The ether-producing temperature is thus seen to be circumscribed within narrow limits; in the old process, however, in which a mixture of equal weights of alcohol and sulphuric acid is subjected to distillation, these conditions can be but partially complied with. At first the temperature of the mixture is too low to yield ether in any quantity, and towards the end of the process, long before all the suphovinic acid has been decomposed, it becomes too high, so that olefiant gas and its accompanying products appear instead. The remedy to this inconvenience consists in restraining the temperature of ebullition of the mixture within its proper bounds by the introduction of a constant supply of alcohol, to combine with the liberated sulphuric acid, and reproduce the sulphovinic acid as fast as it becomes destroyed. The improved, or *continuous* ether-process, in which the same acid is made to etherify an almost indefinite quantity of spirit, may be thus elegantly conducted upon a small scale.

A wide-necked flask is fitted with a sound cork, perforated by three apertures, one of which is destined to receive a thermometer, with the graduation on the stem; a second, the vertical portion of a long narrow tube, terminating in an orifice of about $\frac{1}{20}$ of an inch in diameter; and the third, a wide bent tube, connected with the condenser, to carry off the volatile products. A mixture is made of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine, of about 0·834 sp. gr. This is introduced into the flask, and heated by a lamp. The liquid soon boils, and the thermometer very shortly indicates a temperature of 300° (149°C); when this happens, alcohol of the above density is suffered slowly to enter by the narrow tube, which is put in communication with a reservoir of that liquid, consisting of a large bottle perforated by a hole near the bottom, and furnished with a small brass stop-cock, fitted by a cork; the stop-cock is secured to the end of the long tube by a caoutchouc connecter, tied, as usual with silk cord. As the tube passes nearly to the bottom of the flask, the alcohol gets thoroughly mixed with the acid liquid, the hydrostatic pressure of the

Fig. 166.[1]



column being sufficient to ensure the regularity of the flow; the quan- is easily adjusted by the aid of the stop-cock. For condensation, a g's condenser may be used, supplied with ice-water. The arrangement ured above (fig. 166).

e intensity of heat, and the supply of alcohol, must be so adjusted that hermometer may remain at 300° (149°C), or as near that temperature ssible, while the contents of the flask are maintained in a state of *rapid violent ebullition*—a point of essential importance. Ether and water l over together, and collect in the receiver, forming two distinct strata; mixture slowly blackens, from some slight secondary action of the acid the spirit, or upon the impurities in the latter, but retains, after many of ebullition, its etherifying powers unimpaired. The acid, however, y volatilizes, partly in the state of *oil of wine*, and the quantity of liquid e flask is found, after the lapse of a considerable interval, sensibly nished. This loss of acid constitutes the only limit to the duration of rocess, which might otherwise continue indefinitely.

the large scale, the flask may be replaced by a vessel of lead, the tubes

g. 166. Apparatus for the preparation of ether. *a.* Flask containing the mixture of oil iol and alcohol. *b.* Reservoir with stop-cock, for supplying a constant stream of alcohol. e bent tube connected with the condenser for conveying away the vapours. *d.* The ometer for regulating the temperature of the boiling liquid.

being also of the same metal; the stem of the thermometer may be made to pass air-tight through the cover, and heat may, perhaps, be advantageously applied by high-pressure steam, or hot oil, circulating in a spiral of metal tube, immersed in the mixture of acid and spirit.

The crude ether is to be separated from the water on which it floats, agitated with a little solution of caustic potassa, and re-distilled by the heat of warm water. The aqueous portion, treated with an alkaline solution, and distilled, yields alcohol, containing a little ether. Sometimes the spontaneous separation before mentioned does not occur, from the accidental presence of a larger quantity than usual of undecomposed alcohol; the addition of a little water, however, always suffices to determine it.

We shall once more return to the formation of ether, when we discuss the methyl-compounds.

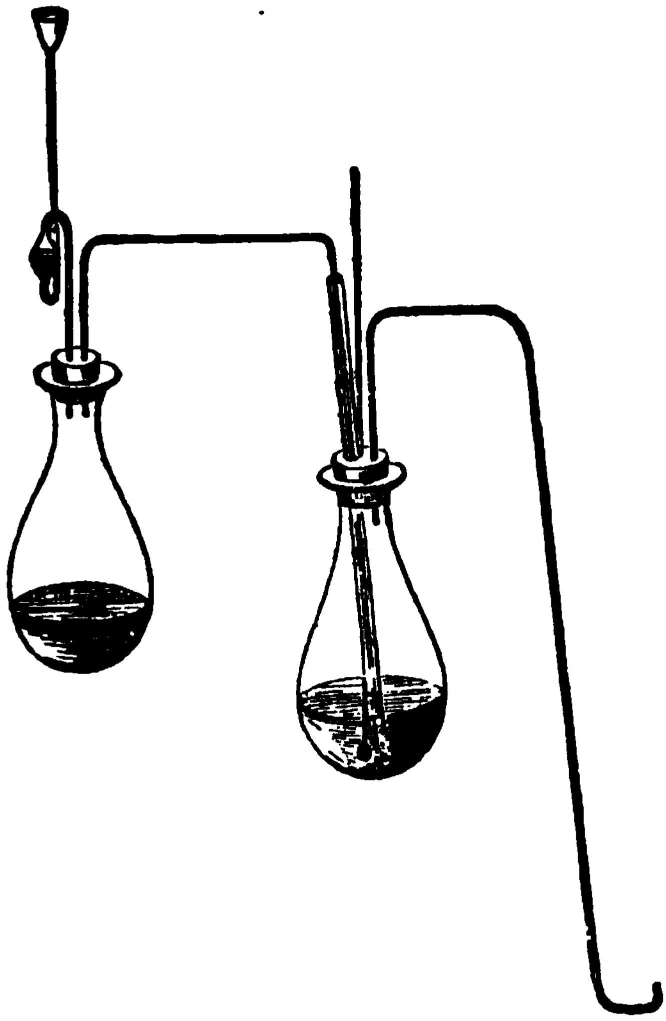
Heavy oil of wine.—When a mixture of 2½ parts of concentrated sulphuric acid, and 1 part of rectified spirit of wine, of 0·833 sp. gr., is subjected to distillation, a little ether comes over, but is quickly succeeded by a yellowish, oily liquid, which may be freed from sulphurous acid by agitation with water, and from ether and undecomposed alcohol by exposure in the vacuum of the air-pump, beside two open capsules, the one containing hydrate of potassa, and the other concentrated sulphuric acid. This substance may be prepared in larger quantity by the destructive distillation of dry sulphovinate of lime; alcohol, oil of wine, and a small quantity of an exceedingly volatile liquid, yet imperfectly examined, are produced. Pure oil of wine is colourless, or greenish, of oily consistence, and heavier than water; it has an aromatic taste, and an odour resembling that of peppermint. Its boiling point is tolerably high. It is soluble in alcohol and ether, but scarcely so in water. By analysis it is found to contain $C_8H_9O,2SO_3$, or perhaps $C_4H_4.SO_3+C_4H_5O,SO_3$; that is, neutral sulphate of ether, in combination with the sulphate of a hydro-carbon, *etherole*.

In contact with boiling water, oil of wine is resolved into sulphovinic acid, and a volatile liquid, known by the name of *light*, or *sweet oil of wine;* with an alkaline solution, this effect is produced even with greater facility. Light oil of wine, left in a cool place for several days, deposits crystals of a white solid matter, which is tasteless, and has but little odour; it is called *etherin*. The fluid residual portion is yellowish, oily, and lighter than water; it has a high boiling-point, solidifies at a very low temperature, and is freely soluble in alcohol and ether; it bears the name of *etherole*. Both etherole and etherin have the same composition, namely C_4H_4, and are consequently isomeric with olefiant gas.

Olefiant gas; ethyline. — This substance may also be advantageously prepared on the principle described, by restraining the temperature within certain bounds, and preventing the charring and destruction of the alcohol, which always occurs in the old process, and which, at the same time, leads to the production of sulphurous and carbonic acids, which contaminate the gas.

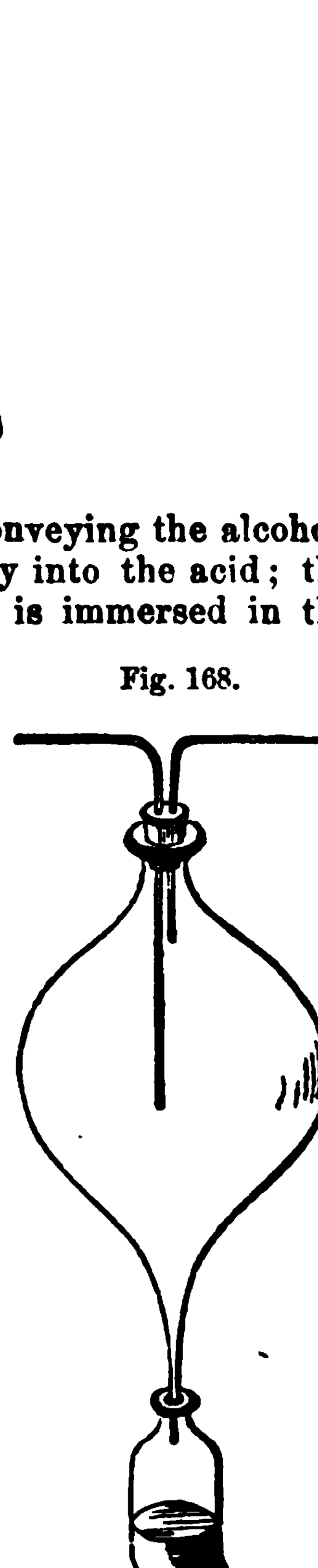
If the vapour of alcohol be passed into somewhat diluted sulphuric acid, maintained at a boiling-heat, it is absorbed with production of sulphovinic acid, which is shortly afterwards decomposed into water and olefiant gas. The process is thus conducted:—A wide-necked flask (fig. 167), containing rectified spirit of wine, is fitted with a cork, through which pass an ordinary safety-tube, with a little water, and the bent glass tube, intended to convey the vapour of the spirit into the acid. The latter must be of such strength, as to have a boiling-point between 320° and 330° (160° and 165°·5C); it is prepared by diluting strong oil of vitriol with rather less than half its weight of water. The acid is placed in a second and larger flask, also closed by a cork, into which are inserted two tubes and a thermometer. The first is a

Fig. 167.



f straight tube, wide enough to allow the tube conveying the alcohol- to pass freely down it, and dipping a little way into the acid; the is a narrow bent tube, the extremity of which is immersed in the of the pneumatic trough. Both flasks are ; and as soon as it is seen that the acid is in a f tranquil ebullition, while the thermometer the temperature above mentioned, the spirit is o boil, and its vapour carried into the acid, very soon begins to evolve olefiant gas and of water, accompanied by a little ether and oil , but no sulphurous acid. The acid liquid does oken, and the experiment may be carried on as s may be desired. This is a very elegant and tive, although somewhat troublesome, method paring the gas. The essential parts of the tus are shown in fig. 167.

Fig. 168.



ORIDE OF OLEFIANT GAS; DUTCH-LIQUID.—It ng been known that when equal measures of t gas and chlorine are mixed over water, absorp- the mixture takes place, and a yellowish oily is produced, which collects upon the surface of ter, and ultimately sinks to the bottom in drops. be easily prepared, in quantity, by causing o gases to combine in a glass globe, fig. 168, a narrow neck at the lower part, dipping into l bottle, destined to receive the product. The ases are conveyed by separate tubes, and t to *mix in the globe*, the olefiant gas being

kept a little in excess. The chlorine should be washed with water, and the olefiant gas passed through strong oil of vitriol, to remove vapour of ether; the presence of sulphurous and carbonic acids is not injurious. Combination takes place very rapidly, and the liquid product trickles down the sides of the globe into the receiver. When a considerable quantity has been collected, it is agitated first with water, and afterwards with concentrated sulphuric acid; it is, lastly, purified by re-distillation. If impure olefiant gas be employed, the crude product contains a large quantity of a substance called by M. Regnault *chloro-sulphuric acid*, SO_2Cl, which, on contact with water, is converted, by the decomposition of the latter, into sulphuric and hydrochloric acids.

Pure Dutch-liquid is a thin, colourless liquid, of agreeably fragrant odour, and sweet taste; it is slightly soluble in water, and readily so in alcohol and ether. It is heavier than water, and boils when heated to 180° (82°·2C); it is unaffected by oil of vitriol and solid hydrate of potassa. When inflamed, it burns with a greenish, smoky light. This substance yields, by analysis, $C_4H_4Cl_2$.

When Dutch-liquid is treated with an alcoholic solution of caustic potassa, it is slowly resolved into chloride of potassium, which separates, and into a new and exceedingly volatile substance, containing C_4H_3Cl, whose vapour requires to be cooled down to 0° (—17°·7C) before it condenses. At that temperature it forms a limpid, colourless liquid. Chlorine is absorbed by this substance, and a compound produced, which contains $C_4H_3Cl_3$; this is in turn decomposed by an alcoholic solution of hydrate of potassa into chloride of potassium and a new volatile liquid, $C_4H_2Cl_2$.

Bromide and iodide of olefiant gas, $C_4H_4Br_2$ and $C_4H_4I_2$.—These compounds correspond to Dutch-liquid; they are produced by bringing olefiant gas in contact with bromine and iodine. The bromide is a colourless liquid, of agreeable, ethereal odour, and has a density of 2·16; it boils at 265° (129°·5C), and solidifies, when cooled, to near 0° (—17°·7C). The iodide is a colourless, crystalline, volatile substance, of penetrating odour; it melts at 174° (78°·8C), resists the action of sulphuric acid, but is decomposed by caustic potassa.

Products of the action of chlorine on Dutch-liquid; chlorides of carbon.—Dutch-liquid readily absorbs chlorine gas, and yields several new compounds, produced by the abstraction of successive portions of hydrogen, and its replacement or substitution by equivalent quantities of chlorine. This regular *substitution* of chlorine, bromine, iodine, &c., in place of hydrogen, as before stated, is a phenomenon of constant occurrence in reactions between these bodies and very many organic compounds. In the present case four such steps may be traced, giving rise, in each instance, to hydrochloric acid and a new substance. Three out of the four new products are volatile liquids, containing $C_4H_3Cl_3$,$C_4H_2Cl_4$ and C_4HCl_5; the fourth C_4Cl_6 in which the substitution of chlorine for hydrogen is complete, is the *chloride of carbon*, long ago obtained by Mr. Faraday by putting Dutch-liquid into a vessel of chlorine gas, and exposing the whole to the influence of light.

Sesquichloride or Perchloride of Carbon, C_4Cl_6, is a white, solid, crystalline substance, of aromatic odour, insoluble in water, but easily dissolved by alcohol and ether; it melts at 320° (160°C), and boils at a temperature a little above. It burns with difficulty, and is unaffected by both acids and alkalis. It is prepared as above stated.

Protochloride of Carbon, C_4Cl_4.—When the vapour of the preceding substance is transmitted through a red-hot porcelain tube filled with fragments of glass or rock-crystal, it is decomposed into free chlorine, and a second chloride of carbon, which condenses in the form of a volatile, colourless

liquid, which has a density of 1·55, and boils at 248° (120°C). The density of its vapour is 5·82. It resembles in chemical relations the perchloride.

Subchloride of Carbon, C_4Cl_2, is produced when the protochloride is passed many successive times through an ignited porcelain tube; it is a white, volatile, silky substance, soluble in ether.

Bichloride of Carbon, C_2Cl_4.—A fourth chloride of carbon is known and will be described here, although it is not derived from the alcohol group. It is formed by passing the vapour of bisulphide of carbon together with chlorine, through a red-hot porcelain-tube. A mixture of chloride of sulphur and bichloride of carbon is formed, which is distilled with potassa, when the chloride of sulphur is decomposed, and pure bichloride passes over. It is a colourless liquid of 1·56 sp. gr., and boils at 170°·6 (77°C). An alcoholic solution of potassa converts this compound into a mixture of chloride of potassium and carbonate of potassa. The same compound is formed by exhausting the action of chlorine upon marsh-gas and chloride of methyl in the sunshine.

COMBUSTIBLE PLATINUM-SALTS OF ZEISE. — A solution of bichloride of platinum in alcohol is mixed with a little chloride of potassium dissolved in hydrochloric acid, and the whole digested some hours at a high temperature. The alcohol is distilled off, the acid residue neutralized by carbonate of potassa, and left to crystallize. The distilled liquid contains hydrochloric ether and aldehyde. The platinum-salt forms yellow, transparent, prismatic crystals, which become opaque on heating from loss of water; when introduced into the flame of a spirit lamp, the salt burns vividly, leaving metallic platinum. It is soluble in 5 parts of warm water. When dried at 212° (100°C), this substance contains Pt_2Cl_2,C_4H_4+KCl. Corresponding compounds, containing Pt_2Cl_2,C_4H_4+NaCl, and $Pt_2Cl_2,C_4H_4+NH_4Cl$, are known to exist.

The chloride of potassium can be separated from the above compound by the cautious addition of bichloride of platinum; the filtered solution yields by evaporation *in vacuo* a yellow, gummy, acid mass. The solution is slowly decomposed in the cold, and rapidly at a boiling heat, with separation of a black precipitate. These compounds are of uncertain constitution.

PRODUCTS OF THE ACTION OF ANHYDROUS SULPHURIC ACID ON ALCOHOL AND OLEFIANT GAS.

When anhydrous alcohol is made to absorb the vapour of anhydrous sulphuric acid, a white, crystalline, solid substance is produced, fusible at a gentle heat, which, when purified from adhering acid, is found to consist of carbon, hydrogen, and the elements of sulphuric acid, in the relation of the equivalent numbers, or probably $C_4H_4,4SO_3$. To this substance Magnus applies the name *sulphate of carbyl*. A body very similar in appearance and properties, and probably identical with this, had previously been produced by M. Regnault, by passing pure and dry olefiant gas over anhydrous sulphuric acid contained in a bent tube.

When the crystals of sulphate of carbyl are dissolved in alcohol, water added, the whole neutralized by carbonate of baryta, and the filtered solution concentrated by very gentle heat to a small bulk, and then mixed with a quantity of alcohol, a precipitate falls, which consists of baryta, in combination with a peculiar acid closely resembling the sulphovinic, but yet differing *in many important* particulars. By the cautious addition of dilute

kept a little in excess. The chlorine should be washed w
olefiant gas passed through strong oil of vitriol, to rem
the presence of sulphurous and carbonic acids is not
tion takes place very rapidly, and the liquid product
of the globe into the receiver. When a considerabl
lected, it is agitated first with water, and afterw
phuric acid: it is, lastly, purified by re-distill
be employed, the crude product contains a l
called by M. Regnault chloro-sulphuric acid,
water, is converted, by the decomposition o
hydrochloric acids.

Pure Dutch-liquid is a thin, colourless
and sweet taste: it is slightly soluble in
ether. It is heavier than water, and
it is unaffected by oil of vitriol and
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analysis, $C_4H_4Cl_2$.

When Dutch-liquid is treated w
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BROMIDE AND IODI
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, and cannot be
tains $C_4H_5O, 2SO_3 + HO$.
ther, as has been already me
sulphate of ethyl (see page
d and several other acids
yet sufficiently studied.

CHLORINE ON ALCOHOL, ETHER, AND
COMPOUNDS.

chlorine is passed into anhydrous alcohol
ed in large quantity, and hydrochloric
ards the end of the process the reaction must
more hydrochloric acid appears, the current
the product agitated with three times its volume
acid: on gently warming this mixture in a water
separates as an oily liquid, which floats on the
purified by distillation from fresh oil of vitriol, and
quantity of quick-lime, which must be kept con
liquid until the end of the operation. Chloral has
by distillation with hydrochloric acid and binoxide

colourless liquid, of peculiar and penetrating odour,
it has but little taste. When dropped upon paper it
which is not, however, permanent. It has a density
at 201°·2 (94°C). Chloral is freely soluble in water,
forms, with a small quantity of water, a solid, crystal-
tion is not affected by nitrate of silver. Caustic baryta
the vapour of chloral when heated in it with appearance
is converted into chloride, carbon is deposited, and car-
Solutions of caustic alkalis also decompose it, with
ormate of the base, and a new volatile liquid, *chloroform.*
$C_4HCl_3O_2$.

preserved for any length of time, even in a vessel herme-
undergoes a very extraordinary change; it becomes con-
solid white, translucent substance, *insoluble chloral*, possessing
same composition as the liquid itself. The new product is but
soluble in water, alcohol, or ether; when exposed to heat, alone
with oil of vitriol, it is re-converted into ordinary chloral. So-
caustic potassa resolves it into formic acid and chloroform. Bro-
upon alcohol in the same manner as chlorine, and gives rise to a
very similar in properties to the foregoing, called bromal, which con-

...crystallizable hydrate with water, and is decom... into formic acid and *bromoform*. A cor... exists.

...non alcohol which contains water; ...hydrochloric acid and *aldehyde*, ...use of the water. With strong ...ts products being a volatile, oily, ...n, long known under the name of

...on pure ether conforms strictly to the ...d; the carbon remains intact, while a ...gen is removed, and its place supplied by ...e. Ether exposed to a current of the dry ..., the temperature being at first artifically ...product, having the odour of fennel. This is ...n $C_4H_3Cl_2O$, or ether, in which 2 eq. of chlorine ... 2 eq. of hydrogen. It may be termed bichlori... ...urther action of chlorine, aided by sunlight, the re...emoved, and a white crystalline solid substance, closely ...loride of carbon produced This is composed of C_4Cl_5O; ...achlorinetted ether. In a substance called *cloretheral*, ...ntally formed by M. d'Arcet, in the preparation of Dutch-...e ether-vapour mixed with the olefiant gas, we have evidently ...ber of this series.

...e compound ethers, the same remarkable law is usually followed. ...ge is, however, often complicated by the appearance of secondary ...s. Thus, *chlorinetted acetic ether*, a dense, oily liquid, very different ...mmon acetic ether, was found to contain $C_8H_6Cl_2O_4$, being a substi...tion product of $C_8H_8O_4{=}C_4H_5O,C_4H_3O_3$; and *chlorinetted formic ether*, ...$H_4Cl_2O_4$, is formed, in like manner, by the substitution of 2 eq. chlorine ...e 2 eq. hydrogen in ordinary formic ether, $C_6H_6O_4{=}C_4H_5O,C_2HO_3$. A ...most remarkable and interesting set of compounds, due to substitution of ...this kind, are formed by the action of chlorine on chloride of ethyl, or light hydrochloric ether. When the vapour of this substance is brought into con...tact with chlorine gas, the two bodies combine to a colourless oily liquid, very like Dutch-liquid, but yet differing from it in several important points; it has, however, precisely the same composition, and its vapour has the same density. By the prolonged action of chlorine three other compounds are successively obtained, each poorer in hydrogen and richer in chlorine than the preceding, the ultimate product being the well-known sesquichloride of carbon of Mr. Faraday.

Hydrochloric ether	C_4H_5Cl
Monochlorinetted hydrochloric ether	$C_4H_4Cl_2$
Bichlorinetted	$C_4H_3Cl_3$
Trichlorinetted	$C_4H_2Cl_4$
Quadrichlorinetted	$C_4H\ Cl_5$
Sesquichloride of carbon	$C_4\ \ Cl_6$

DERIVATIVES OF ALCOHOL CONTAINING SULPHUR.

MERCAPTAN.—A solution of caustic potassa, of 1·28 or 1·3 sp. gr., is satu...rated with sulphuretted hydrogen, and mixed in a retort with an equal volume of *solution of sulphovinate of lime* of the same density. The retort is con-

soluble in alcohol, and separating from that liquid in distinct cryst
contain C_4H_5S,HgS. This compound is decomposed by sulphurett
gen, sulphide of mercury being thrown down, and mercaptan re
By adding solutions of the oxides of lead, copper, silver, and g
alcoholic solution of mercaptan, corresponding compounds contain
metals are formed. Caustic potassa produces no effect upon merca
potassium displaces hydrogen, and gives rise to a crystallizable c
soluble in water.

XANTHIC ACID.—The elements of ether and those of bisulphide
combine in presence of an alkali to a very extraordinary substance
ing the properties of an oxygen-acid, to which the name *xanthic* i
on account of the yellow colour of one of its most permanent an
teristic salts, that of oxide of copper. Hydrate of potassa is dis
12 parts of alcohol of 0·800 sp. gr.; into this solution bisulphide
is dropped until it ceases to be dissolved, or until the liquid loses
linity. The whole is then cooled to 0° (—17°·8C), when the po
separates in the form of brilliant, slender, colourless prisms, which
quickly pressed between folds of bibulous paper, and dried *in vac*
freely soluble in water and alcohol, but insoluble in ether, and is
destroyed by exposure to air by oxidation of a part of the sulph
drated xanthic acid may be prepared by decomposing the forego
pound by dilute sulphuric or hydrochloric acid. It is a colour
liquid, heavier than water, of powerful and peculiar odour, and
bustible; it reddens litmus-paper, and ultimately bleaches it. E
gentle heat, it is decomposed into alcohol and bisulphide of carl
happens at a temperature of 75° (23°·8C). Exposed to the air, or
neath the surface of water open to the atmosphere, it becomes cov
a whitish crust, and is gradually destroyed. The xanthates of t
and of baryta are colourless and crystallizable; the lime-salt drie
gummy mass; the xanthates of the oxides of zinc, lead, and me
white, and but feebly soluble, that of copper is a flocculent, insol
stance, of beautiful yellow colour.

Hydrated xanthic acid contains C H S O,HO; or C H O,C S ,HO

id, to which Dr. Frankland has given the name *zinc-ethyl*. It may be rated from the residue by distilling it in a current of hydrogen, when it obtained in the form of a liquid of a disagreeable odour, which contains $_{5}$Zn. In contact with atmospheric air it is rapidly oxidized. When ed with water, this compound is decomposed with evolution of a carbo-ed hydrogen, having the formula $C_4H_6 = C_4H_5,H$, which may be viewed e hydride of ethyl.

:IBETHYL.—Iodide of ethyl when distilled with an alloy of antimony and ssium, yields a curious substance, which MM. Loewig and Schweizer described under the name of stibethyl. It contains $SbC_{12}H_{15} = Sb\ 3$ $[_{5})$. We shall return to this substance when speaking of the compound onias.[1]

PRODUCTS OF THE OXIDATION OF ALCOHOL.

hen alcohol and ether burn with flame in free air, the products of their oustion are, as with all bodies of like chemical nature, carbonic acid and r. Under peculiar circumstances, however, these substances undergo ial oxidation, in which the hydrogen alone is affected, the carbon re-ding untouched. The result is the production of certain compounds, h form a small series, supposed by some chemists to contain a common al, to which the name *acetyl* is applied. It is derived from ethyl by the ation and removal of 2 eq. of hydrogen.

Table of Acetyl-Compounds.

Acetyl (symbol Ac)	C_4H_3
Oxide of acetyl (unknown)	C_4H_3O
Hydrate of oxide of acetyl; aldehyde	C_4H_3O,HO
Acetylous acid; aldehydic acid	$C_4H_3O_2,HO$
Acetylic acid; acetic acid	$C_4H_3O_3,HO$

etyl and its protoxide are alike hypothetical.

DEHYDE, $C_4H_4O_2$ or AcO,HO.—This substance is formed, as already no-l, among other products, when the vapour of ether or alcohol is trans-ed through a red-hot tube; also, by the action of chlorine on weak iol. It is best prepared by the following process: — 6 parts of oil of ol are mixed with 4 parts of rectified spirit of wine, and 4 parts of r; this mixture is poured upon 6 parts of powdered binoxide of man-se, contained in a capacious retort, in connection with a condenser, d by ice-cold water. Gentle heat is applied; and when 6 parts of liquid passed over, the process is interrupted. The distilled product is put a small retort, with its own weight of chloride of calcium, and redis-l; the operation is repeated. The aldehyde, still retaining alcohol, and impurities, is mixed with twice its volume of ether, and saturated dry ammoniacal gas; a crystalline compound of aldehyde and ammonia rates, which may be washed with a little ether, and dried in the air. this substance the aldehyde may be separated by distillation in a r-bath, with sulphuric acid, diluted with an equal quantity of water; areful rectification from chloride of calcium, at a temperature not ex-ng 87° (30°·5C), it is obtained pure and anhydrous.

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[1] musethyl, $BiC_{12}H_{15} = Bi\ 3(C_4H_5)$. Stanethyl, SnC_4H_5 and tellurethyl, TeC_4H_5 have also *produced by similar reactions and* some of their compounds investigated.—R. B.

Aldehyde[1] is a limpid, colourless liquid, of characteristic ethereal odour, which, when strong, is exceedingly suffocating. It has a density of 0·790, boils at 72° (22°·8C), and mixes, in all proportions, with water, alcohol, and ether; it is neutral to test-paper, but acquires acidity on exposure to air, from the production of acetic acid; under the influence of platinum-black this change is very speedy. When a solution of this compound is heated with caustic potassa, a remarkable brown, resin-like substance is produced, the so-called *aldehyde-resin*. Gently heated with protoxide of silver, it reduces the latter without evolution of gas, the metal being deposited on the inner surface of the vessel as a brilliant and uniform film; the liquid contains aldehydate of silver.

When treated with hydrocyanic acid, aldehyde yields a substance called *alanine*, which was already noticed, when treating of lactic acid, and which will be described more in detail in the section on vegeto-alkalis, under the head of bases from aldehyde.

The action of sulphuretted hydrogen upon the ammonia-compound gives rise to the formation of *thialdine*, noticed likewise under the head of bases from aldehyde.

The ammonia-compound above mentioned forms transparent, colourless crystals of great beauty; it has a mixed odour of ammonia and turpentine; it dissolves very easily in water, with less facility in alcohol, and with difficulty in ether; it melts at about 170° (76°C), and distils unchanged at 212° (100°C). Acids decompose it, with production of ammoniacal salt and separation of aldehyde. The crystals, which are apt to become yellow, and lose their lustre in the air, contain $C_4H_4O_2+NH_3$.

When pure aldehyde is long preserved in a close-stopped vessel, it is sometimes found to undergo spontaneous change into one, and even two isomeric modifications, differing completely in properties from the original compound. In a specimen kept some weeks at 32° (0°C), transparent acicular crystals were observed to form in considerable quantity, which, at a temperature little exceeding that of the freezing-point of water, melted to a colourless liquid, miscible with water, alcohol, and ether; a few crystals remained, which sublimed without fusion, and were probably composed of the second substance. This new body received the name *elaldehyde;* it was found to be identical in composition with aldehyde, but to differ in properties and in the density of its vapour; the latter has a sp. gr. of 4·515, while that of aldehyde is only 1·532, or one-third of that number. It refuses to combine with ammonia, is not rendered brown by potassa, and is but little affected by solution of silver.

The second modification, or *metaldehyde*, is sometimes produced in pure aldehyde, kept at the common temperature of the air, even in hermetically-sealed tubes; the conditions of its formation are unknown. It forms colourless, transparent, prismatic crystals, which sublime without fusion at a temperature above 212° (100°), and are soluble in alcohol and ether, but not in water. They also were found, by analysis, to have the same composition as aldehyde. The substance which we have described by the term of *chloral* may be viewed as bichlorinetted aldehyde.

ALDEHYDIC ACID, $C_4H_3O_2,HO$. — When solution of aldehydate of silver, obtained by digesting oxide of silver in excess with aldehyde, is precipitated by sulphuretted hydrogen, an acid liquid is obtained, which neutralizes alkalis, and combines with the oxides of the metals. It is very easily decomposed. Aldehydate of silver, mixed with baryta-water, gives rise to aldehydate of baryta and oxide of silver: if this precipitate be heated in the liquid,

[1] *Alcohol dehydrogenatus.*

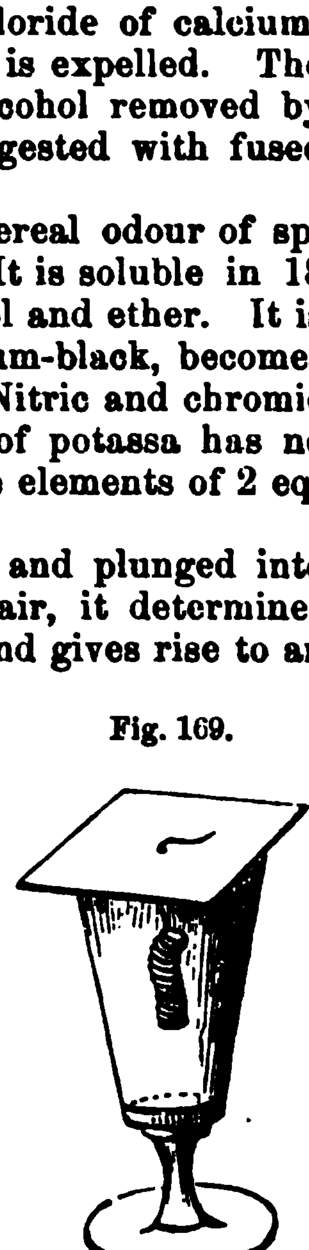
he metal is reduced, and neutral acetate of baryta formed; whence it is inferred that the new acid contains the elements of the acetic acid, *minus* an equivalent of oxygen.

ACETAL.—This substance is one of the products of the slow oxidation of alcohol-vapour under the influence of platinum-black. Spirit of wine is poured into a large, tall, glass-jar, to the depth of about an inch, and a shallow capsule, containing slightly-moistened platinum-black, arranged above the surface of the liquid; the jar is loosely covered by a glass plate, and left during two or three weeks, in a warm situation. At the expiration of that period the liquid is found highly acid; it is to be neutralized with carbonate of potassa, as much chloride of calcium added as the liquid will dissolve, and the whole subjected to distillation, the first fourth only being collected. Fused chloride of calcium added to the distilled product now throws up a light oily liquid, which is a mixture of acetal with alcohol, aldehyde, and acetic ether. By fresh treatment with chloride of calcium, and long exposure to gentle heat in a retort, the aldehyde is expelled. The acetic ether is destroyed by caustic potassa, and the alcohol removed by washing with water, after which the acetal is again digested with fused chloride of calcium, and re-distilled.

Pure acetal is a thin, colourless fluid, of agreeable ethereal odour of sp. gr. 0·821 at 72° (22°·2C), and boiling at 220° (104°C). It is soluble in 18 parts of water, and miscible in all proportions with alcohol and ether. It is unchanged in the air; but, under the influence of platinum-black, becomes converted into aldehyde, and eventually into acetic acid. Nitric and chromic acids produce a similar effect. Strong boiling solution of potassa has no action on this substance. Acetal contains $C_{12}H_{14}O_4$, or the elements of 2 eq. ether and 1 eq. aldehyde, $C_{12}H_{14}O_4=2C_4H_5O+C_4H_4O_2$.

When a coil of fine platinum wire is heated to redness, and plunged into a mixture of ether, or alcohol-vapour and atmospheric air, it determines upon its surface the partial combustion of the former, and gives rise to an excessively pungent acrid vapour, which may be condensed to a colourless liquid by suitable means. The heat evolved in the act of oxidation is sufficient to maintain the wire in an incandescent state. The experiment may be made by putting a little ether into an ale-glass, fig. 169, and suspending over it the heated spiral from a card; or by slipping the coil over the wick of a spirit-lamp, so that the greater part may be raised above the cotton; the lamp is supplied with ether or spirit of wine, lighted for a moment, and then blown out. The coil continues to glow in the mixed atmosphere of air and combustible vapour, until the ether is exhausted. This is the *lamp without flame* of Sir H. Davy. A ball of spongy platinum may be substituted for the coil of wire. The condensed liquid contains acetic and formic acids with aldehyde and aldehydic acid.

Fig. 169.



ACETIC ACID.—Pure alcohol, exposed to the air, or thrown into a vessel of oxygen gas, fails to suffer the slightest change by oxidation; when diluted with water, it remains also unaffected. If, on the other hand, spirit of wine be dropped upon dry platinum-black, the oxygen condensed into the pores of the latter, reacts so powerfully upon the alcohol as to cause its instant inflammation. When the spirit is mixed with a little water, and slowly dropped upon the finely divided metal, oxidation still takes place, but with less energy, and vapour of acetic acid is abundantly evolved. It is almost unnecessary to add, that the platinum itself undergoes no change in this experiment.

Dilute alcohol, mixed with a little yeast, or almost any oxidized organic matter, susceptible of putrefaction, and exposed to the air, speedily becomes oxidized to acetic acid. Acetic acid is thus manufactured in Germany, by suffering such a mixture to flow over wood-shavings, steeped in a little vinegar, contained in a large cylindrical vessel, through which a current of air is made to pass. The greatly extended surface of the liquid expedites the change, which is completed in a few hours. No carbonic acid is produced in this reaction.

The best vinegar is made from wine by spontaneous acidification in a partially filled cask to which the air has access. Vinegar is first introduced into the empty vessel, and a quantity of wine added; after some days a second portion of wine is poured in, and after similar intervals a third and a fourth. When the whole has become vinegar, a quantity is drawn off equal to that of the wine employed, and the process is recommenced. The temperature of the building is kept up to 86° (30°C). Such is the plan adopted at Orleans.[1] In England vinegar of an inferior description is prepared from a kind of beer made for the purpose. The liquor is exposed to the air in half-empty casks, loosely stopped, until acidification is complete. A little sulphuric acid is afterwards added, with a view of checking further decomposition, or *mothering*, by which the product would be spoiled.

There is another source of acetic acid besides the oxidation of alcohol: when dry, hard wood, as oak and beech, is subjected to destructive distillation at a red-heat, acetic acid is found among the liquid condensable products of the operation. The distillation is conducted in an iron cylinder of large dimensions, to which a worm or condenser is attached; a sour watery liquid, a quantity of tar, and much inflammable gas pass over, while charcoal of excellent quality remains in the retort. The acid liquid is subjected to distillation, the first portion being collected apart for the sake of a peculiar volatile body, shortly to be described, which it contains. The remainder is saturated with lime, concentrated by evaporation, and mixed with solution of sulphate of soda; sulphate of lime precipitates, while the acetic acid is transferred to the soda. The filtered solution is evaporated to its crystallizing-point; the crystals are drained as much as possible from the dark, tarry mother-liquid, and deprived by heat of their combined water. The dry salt is then cautiously fused, by which the last portions of tar are decomposed or expelled; it is then re-dissolved in water, and re-crystallized. Pure acetate of soda, thus obtained, readily yields hydrated acetic acid by distillation with sulphuric acid.

The strongest acetic acid is prepared by distilling finely powdered anhydrous acetate of soda with three times its weight of concentrated oil of vitriol. The liquid is purified by rectification from sulphate of soda, accidentally thrown up, and then exposed to a low temperature. Crystals of hydrate of acetic acid form in large quantity, which may be drained from the weaker fluid portion, and then suffered to melt. Below 60° (15°·5C) this substance forms large, colourless, transparent crystals, which above that temperature fuse to a thin, colourless liquid, of exceedingly pungent and well-known odour; it raises blisters on the skin. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. When diluted it has a pleasant acid taste. The hydrate of acetic acid in the liquid condition has a density of 1·063, and boils at 246° (119°C); its vapour is inflammable. Acetic acid forms a great number of exceedingly important salts, all of which are soluble in water; the acetates of silver and mercury are the least soluble.

The hydrate of acetic acid contains $C_4H_3O_3,HO = AcO_3,HO$; it is formed

[1] Dumas, Chimie appliquée aux Arts, vi. 557.

om alcohol by the substitution of 2 eq. of oxygen for 2 eq. of hydrogen. he water is *basic*, and can be replaced by metallic oxides. A different view garding the constitution of this acid has been proposed by Prof. Kolbe; it chiefly based upon the remarkable decomposition which acetic acid under-es when submitted to the action of the galvanic current. We shall return this subject when speaking of valerianic acid.

Dilute acetic acid, or distilled vinegar, used in pharmacy, should always carefully examined for copper and lead; these impurities are contracted om the metallic vessel or condenser sometimes employed in the process. he strength of any sample of acetic acid cannot be safely inferred from its nsity, but is easily determined by observing the quantity of dry carbonate soda necessary to saturate a known weight of the liquid.[1]

ACETATE OF POTASSA, $KO,C_4H_3O_3$.—This salt crystallizes with great diffi-ilty; it is generally met with as a foliated, white, crystalline mass, obtained neutralizing carbonate of potassa by acetic acid, evaporating to dryness, d heating the salt to fusion. The acetate is extremely deliquescent, and luble in water and alcohol; the solution is usually alkaline, from a little s of acid by the heat to which it has been subjected. From the alcoholic lution, carbonate of potassa is thrown down by a stream of carbonic acid.

ACETATE OF SODA, $NaO,C_4H_3O_3+6HO$.—The mode of preparation of this lt on the large scale has been already described; it forms large, transpa-ent, colourless crystals, derived from a rhombic prism, which are easily ndered anhydrous by heat, effloresce in dry air, and dissolve in 3 parts of old, and in an equal weight of hot water,—it is also soluble in alcohol. The ste of this substance is cooling and saline. The dry salt undergoes the aseous fusion at 550° (287°·8C), and begins to decompose at 600° (315°·5C).

ACETATE OF AMMONIA; SPIRIT OF MINDERERUS; $NH_4O,C_4H_3O_3$.—The neu-ral solution obtained by saturating strong acetic acid by carbonate of am-monia cannot be evaporated without becoming acid from loss of base; the alt passes off in large quantity with the vapour of water. Solid acetate of mmonia is best prepared by distilling a mixture of equal parts of acetate of ime and powdered salammoniac; chloride of calcium remains in the retort. A saturated solution of the solid salt in hot water, suffered slowly to cool in a close vessel, deposits long slender crystals, which deliquesce in the air. Acetate of ammonia has a sharp and cooling, yet sweet, taste; its solution becomes alkaline on keeping, from decomposition of the acid.

Acetate of ammonia when distilled with anhydrous phosphoric acid, loses 4 eq. of water, being converted into a colourless liquid inmiscible with water, of an aromatic odour, and boiling at 170° (77°C) which has received the name of *acetonitrile* C_4H_3N. When boiled with acids or alkalis it re-assimi-lates the 4 eq. of water, being converted again into acetic acid and ammonia. This substance is the type of a class; great many ammonia-salts of acids, analagous to acetic acid, undergoing a similar change when treated with an-hydrous phosphoric acid. It is likewise obtained by a perfectly different process, which will be described when treating of the methyl-compounds. (See cyanide of methyl, page 383, and also acetic ether, page 356.)

The acetates of *lime*, *baryta*, and *strontia* are very soluble, and can be pro-cured in crystals; acetate of *magnesia* crystallizes with difficulty.

ACETATE OF ALUMINA, $Al_2O_3,3C_4H_3O_3$.—This salt is very soluble in water, and dries up in the vacuum of the air-pump to a gummy mass, without trace

[1] Acetic acid increases in density by the addition of water, and reaches its maximum 1.079 when 30 parts have been mixed with 100 of the strongest acid; it then decreases in density, and when 135 parts have been added its specific gravity is the same as the hydrate, 1.063° The most ready method to test its strength is to suspend in it a fragment of pure marble of known weight; the loss of weight resulting will be five-sixths of the weight of the hydrated acid present, *50 parts of carbonate of* lime being required to saturate 60 parts of acetic acid.—*R. B.*

white needles, very prone to oxidation; both salts dissolve freel
Acetate of sesquioxide of iron is a dark-brownish red, uncrystalliza
of powerful astringent taste. *Acetate of cobalt* forms a violet-colo
talline, deliquescent mass. The *nickel-salt* separates in green crys
dissolve in 6 parts of water.

ACETATE OF LEAD, PbO, $C_4H_3O_3+3HO$.—This important salt i
on a large scale by dissolving litharge in acetic acid; it may be o
colourless, transparent, prismatic crystals, but is generally met w
merce as a confusedly crystalline mass, somewhat resembling
From this circumstance, and from its sweet taste, it is often calle
lead. The crystals are soluble in about $1\frac{1}{2}$ parts of cold water, e
dry air, and melt when gently heated in their water of crystalli
latter is easily driven off, and the anhydrous salt obtained, which
igneous fusion, and afterwards decomposes, at a high temperatur
of lead is soluble in alcohol. The watery solution has an inten
and at the same time astringent, taste, and is not precipitated by
It is an article of great value to the chemist.

BASIC ACETATES (SUBACETATES) OF LEAD. — *Sesqui-basic acetate* i
when the neutral anhydrous salt is so far decomposed by heat as
converted into a porous white mass, decomposable only at a m
temperature. It is soluble in water, and separates from the solu
rated to a syrupy consistence in the form of crystalline scales.
$3PbO,2C_4H_3O_3$. A sub-acetate with 3 eq. of base is obtained by d
a moderate heat 7 parts of finely-powdered litharge, 6 parts of
lead, and 30 parts of water. Or, by mixing a cold saturated solut
tral acetate with a fifth of its volume of caustic ammonia, and l
whole some time in a covered vessel; the salt separates in minu
which contain $3PbO,C_4H_3O_3+HO$. The solution of sub-acetate p
the first method is known in pharmacy under the name of *Go*
A third sub-acetate exists, formed by adding a great excess of am
solution of acetate of lead, or by digesting acetate of lead with a l
tity of oxide. It is a white, slightly crystalline substance, insolu
and but little soluble in boiling water. It contains $6PbO,C_4H_3O_3$

Basic acetates (sub-acetates) of copper. — Common verdigris, made spreading the marc of grapes upon plates of copper exposed to the air ring several weeks, or by substituting, with the same view, pieces of cloth pped in crude acetic acid, is a mixture of several basic acetates of copper ich have a green or blue colour. One of these, $3CuO,2C_4H_3O_3+6HO$, is tained by digesting the powdered verdigris in warm water, and leaving the luble part to spontaneous evaporation. It forms a blue, crystalline mass, t little soluble in cold water. When boiled, it deposits a brown powder, ich is a sub-salt with large excess of base. The green insoluble residue the verdigris contains $3CuO,C_4H_3O_3+3HO$: it may be formed by digesting utral acetate of copper with the hydrated oxide. By ebullition with water is resolved into neutral acetate and the brown sub-salt.

Acetate of silver, $AgO,C_4H_3O_3$, is obtained by mixing acetate of potassa th nitrate of silver, and washing the precipitate with cold water to remove e nitrate of potassa. It crystallizes from a warm solution in small colourss needles, which have but little solubility in the cold.

Acetate of suboxide of mercury forms small scaly crystals, which are as feebly luble as those of acetate of silver. The salt of the *red oxide of mercury* dislves with facility.

Chloracetic acid. — When a small quantity of crystallizable acetic acid introduced into a bottle of dry chlorine gas, and the whole exposed to the rect solar rays for several hours, the interior of the vessel is found coated ith a white crystalline substance, which is a mixture of the new product, e chloracetic acid, with a small quantity of oxalic acid. The liquid at the ttom contains the same substances, together with the unaltered acetic acid. ydrochloric and carbonic acid gases are at the same time produced, together ith suffocating vapour, resembling chloro-carbonic acid. The crystalline atter is dissolved out with a small quantity of water, added to the liquid ntained in the bottle, and the whole placed in the vacuum of the air-pump, ith capsules containing fragments of caustic potassa, and concentrated sulric acid. The oxalic acid is first deposited, and afterwards the new subance in beautiful rhombic crystals. If the liquid refuses to crystallize, it ay be distilled with a little anhydrous phosphoric acid, and then evaporated. he crystals are spread upon bibulous paper to drain, and dried *in vacuo.*

Chloracetic acid is a colourless and extremely deliquescent substance; it as a faint odour, and a sharp, caustic taste, bleaching the tongue and stroying the skin; the solution is powerfully acid. At 115° (46°C) it elts to a clear liquid, and at 390° (218°·8C) boils and distils unchanged. he density of the fused acid is 1·617; that of the vapour, which is very irriting, is probably 5·6. The substance contains, according to the analysis f M. Dumas, $C_4Cl_3O_3,HO$, or the elements of hydrated acetic acid from hich 3 eq. of hydrogen have been withdrawn, and 3 eq. of chlorine substited.

Chloracetic acid forms a variety of salts, which have been examined and scribed: it combines also with ether, and with the ether of wood-spirit. hese compounds correspond to the ethers of the other organic acid. *Chloratate of potassa* crystallizes in fibrous, silky needles, which are permanent the air, and contain $KO,C_4Cl_3O_3+HO$. The *ammoniacal* salt is also crysllizable and neutral; it contains $NH_4O,C_4Cl_3O_3+5HO$. *Chloracetate of silver* a soluble compound, crystallizing in small greyish scales, which are easily tered by light; it gives, on analysis, $AgO,C_4Cl_3O_3$, and is consequently hydrous.

When chloracetic acid is boiled with an excess of ammonia, it is decomsed, with production of chloroform and carbonate of ammonia.

$$C_4HCl_3O_4 = C_2HCl_3 \text{ and } C_2O_4.$$

Heat is then applied to the retort, which is gradually increased to redness. At the close of the operation, the receiver is found to contain two liquids besides a quantity of reduced arsenic: the heavier of these is the oxide of kakodyl in a coloured and impure condition; the other chiefly consists of water, acetic acid, and acetone. The gas given off during distillation is principally carbonic acid. The crude oxide of kakodyl is repeatedly washed by agitation with water, previously freed from air by boiling, and afterwards re-distilled from hydrate of potassa in a vessel filled with pure hydrogen gas. All these operations must be conducted in the open air, and the strictest precautions adopted to avoid the accidental inhalation of the smallest quantity of the vapour or its products.

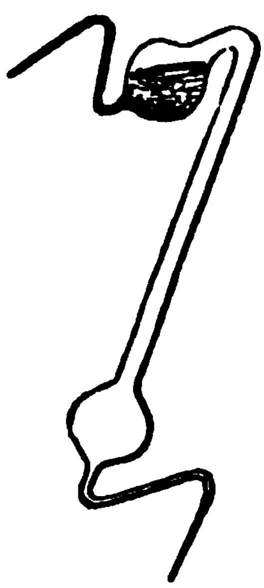
Oxide of kakodyl is a colourless, ethereal liquid of great refractive power; it is much heavier than water, having a density of 1·462. It is very slightly soluble in water, but easily dissolved by alcohol; its boiling-point approaches 302° (150°C), and it solidifies to a white crystalline mass at 9° (—12°C). The odour of this substance is extremely offensive, resembling that of arseniuretted hydrogen: the minutest quantity attacks the eyes and the mucous membrane of the nose; a larger dose is highly dangerous. When exposed to the air, oxide of kakodyl emits a dense white smoke, becomes heated, and eventually takes fire, burning with a pale flame, and producing carbonic acid, water, and a copious cloud of arsenious acid. It explodes when brought into contact with strong nitric acid, and inflames spontaneously when thrown into chlorine gas. The density of the vapour of this body is about 7·5. Oxide of kakodyl is generated by the reaction of arsenious acid on the elements of acetone, carbonic acid being at the same time formed; the accompanying products are accidental:—

2 eq. acetone $C_6H_6O_2$, and 1 eq. arsenious acid, AsO_3 = 1 eq. oxide kakodyl, C_4H_6AsO, and 2 eq. carbonic acid, C_2O_4.

Chloride of Kakodyl, KdCl. — A dilute alcoholic solution of oxide of kakodyl is cautiously mixed with an equally dilute solution of corrosive sublimate, avoiding an excess of the latter; a white, crystalline, inodorous precipitate falls, containing KdO+2HgCl; when this is distilled with concentrated liquid hydrochloric acid, it yields corrosive sublimate, water, and *chloride of kakodyl*, which distils over. The product is left some time in contact with chloride of calcium and a little quicklime, and then distilled alone in an atmosphere of carbonic acid. The pure chloride is a colourless liquid, which does not fume in the air, but emits a vapour even more fearful in its effects, and more insupportable in odour than that of the oxide. It is heavier than water, and insoluble in that liquid, as also in ether; alcohol, on the other hand, dissolves it with facility. The boiling-point of this compound is a little above 212° (100°C); its vapour is colourless, is spontaneously inflammable in the air, and has a density of 4·56. Dilute nitric acid dissolves the chloride without change; with the concentrated acid ignition and explosion occur. Chloride of kakodyl combines with subchloride of copper to a white, insoluble, crystalline double salt, containing $KdCl+Cu_2Cl$, and also with oxide of kakodyl.

Kakodyl, in a free state, may be obtained by the action of metallic zinc, iron, or tin upon the above-described compound. Pure and anhydrous chloride of kakodyl is digested for three hours, at a temperature of 212° (100°C), with slips of clean metallic zinc contained in a bulb blown upon a glass tube, previously filled with carbonic acid gas, and hermetically sealed. The metal dissolves quietly without evolution of gas. When the action is complete, and the whole cool, the vessel is observed to contain a white saline mass, which on the admission of a little water dissolves, and liberates a *heavy oily* liquid, the kakodyl itself. This is rendered quite pure by distillation from a fresh quantity of zinc, the process being conducted in the little

Fig. 170.



ıtus shown in the margin (fig. 170), which is made ı piece of glass tube, and is intended to serve the pur- oth of retort and receiver. The zinc is introduced ıe upper bulb, and then the tube drawn out in the r represented. The whole is then filled with carbonic ınd the lower extremity put into communication with ı hand-syringe. On dipping the point *a* into the crude yl and making a slight movement of exhaustion, the is drawn up into the bulb. Both extremities are ealed in the blow-pipe flame, and after a short diges- ; 212° (100°C) or a little above, the pure kakodyl is ıd off into the lower bulb, which is kept cool. It a colourless, transparent, thin liquid, much resemb- ıe oxide in odour, and surpassing that substance in mability. When poured into the air, or into oxygen ignites instantly; the same thing happens with chlo- With very limited access of air it throws off white fumes, passing into and eventually into kakodylic acid. Kakodyl boils at 338° (170°C), hen cooled to 21° (—6°·1C) crystallizes in large, transparent, square ι. It combines directly with sulphur and chlorine, and in fact may 7 be made to furnish all the compounds previously derived from the It constitutes the most perfect type of an organic *quasi*-metal which stry yet possesses.

odyl is decomposed by a temperature inferior to redness into metallic ɛ, and a mixture of 2 measures light carbonetted hydrogen, and 1 re olefiant gas.

ɔride of kakodyl forms a *hydrate*, which is thick and viscid, and readily posable by chloride of calcium, which withdraws the water. In the :ation of the chloride, and also in other operations, a small quantity of amorphous powder is often obtained, called *erytrarsin*. This is inso- n water, alcohol, ether, and caustic potassa, but is gradually oxidized posure to the air, with production of arsenious acid. It contains $_3As_2$.

ɪᴅᴇ ᴏғ ᴋᴀᴋᴏᴅʏʟ, KdI. — This is a thin, yellowish liquid, of offensive and considerable specific gravity, prepared by distilling oxide of yl with strong solution of hydriodic acid. A yellow crystalline sub- is at the same time formed, which is an oxy-iodide. *Bromide* and *le* of kakodyl have likewise been obtained and examined.

ᴘʜɪᴅᴇ ᴏғ ᴋᴀᴋᴏᴅʏʟ, KdS, is prepared by distilling chloride of kakodyl solution of the bisulphide of barium and hydrogen. It is a clear, thin, less liquid, smelling at once of alkarsin and mercaptan, insoluble in and spontaneously inflammable in the air. Its boiling-point is high, distils easily with the vapour of water. This substance dissolves ır, and generates tersulphide of kakodyl, KdS_3, which is a sulphur- ınd combines with the sulphides of gold, copper, bismuth, lead, and ɔny.

ɴɪᴅᴇ ᴏғ ᴋᴀᴋᴏᴅʏʟ, KdCy. — The cyanide is easily formed by distilling in with strong hydrocyanic acid, or cyanide of mercury. Above 91° C) it is a colourless, ethereal liquid, but below that temperature it llizes in colourless, four-sided prisms, of beautiful diamond lustre. It ,t about 284° (140°C), and is but slightly soluble in water. It requires heated before inflammation occurs. The vapour of this substance is earfully poisonous; the atmosphere of a room is said to be so far con- ıted by the evaporation of a few grains, as to cause instantaneous ıess of the hands and feet, vertigo, and even unconsciousness.

:ᴏᴅʏʟɪᴄ ᴀᴄɪᴅ (*ᴀʟᴋᴀʀɢᴇɴ*); KdO_3.—This is the ultimate product of the

with alkalis and evaporated, a gummy, amorphous mass results. oxides of silver and mercury, on the other hand, it yields crystalli pounds. It unites with oxide of kakodyl, and forms a variety of co with metallic salts. Alkargen is exceedingly stable; it is neither red, fuming nitric acid, aqua regia, nor even chromic acid in s may be boiled with these substances without the least change. dized, however, by phosphorous acid and protochloride of tin t kakodyl. Dry hydriodic acid gas decomposes it, with productio iodide of kakodyl, and free iodine; hydrochloric acid, under simi stances, converts it into a corresponding terchloride, which is soli tallizable. Lastly, what is extremely remarkable, this substanc the least degree poisonous.

PARAKAKODYLIC OXIDE. — When air is allowed access to a alkarsin, so slowly that no sensible rise of temperature follows, t gradually converted into a thick syrupy liquid, full of crystals o acid. Long exposure to air, or the passage of a copious current mass, heated to 158° (70°C), fails to induce crystallization of the in this state water be added, everything dissolves, and a solu which contains kakodylic acid, partly free, and partly in combi the oxide of kakodyl. When this liquid is distilled, water, havin of alkarsin, passes over, and afterwards an oily liquid, which compound. Impure kakodylic acid remains in the retort.

Parakakodylic oxide, purified by rectification from caustic colourless, oily liquid, strongly resembling alkarsin itself in odo to solvents, and in the great number of its reactions. It neith the air, however, nor takes fire at common temperatures; its va with air, and heated to 190° (87°·8C), explodes with violence. 't is found to have exactly the same composition as ordinary oxide

SECTION II.

BSTANCES MORE OR LESS ALLIED TO ALCOHOL.

WOOD-SPIRIT AND ITS DERIVATIVES.

ear 1812, Mr. P. Taylor discovered, among the liquid products ructive distillation of dry-wood, a peculiar volatile inflammable h resembling spirit of wine, to which allusion has already been s substance has been shown by MM. Dumas and Péligot to be ond alcohol, forming an ether, and a series of compounds, exactly ng with those of vinous spirit, and even more complete, in some the latter. Wood-spirit, like ordinary alcohol, may be regarded d oxide of a body like ethyl, containing C_2H_3, called *methyl.*[1] reat number of compound methyl-ethers have been described; t the most complete parallelism of origin, properties, and consti- those derived from common alcohol.

Wood-spirit Series.

yl (symbol, Me)	C_2H_3
of methyl	C_2H_3O
ide of methyl (marsh gas)	C_2H_3H
ide of methyl	C_2H_3Cl
e of methyl &c	C_2H_3I
methyl	C_2H_3Zn
-spirit	C_2H_3O,HO
ate of oxide of methyl	C_2H_3O,SO_3
te of oxide of methyl &c	C_2H_3O,NO_5
omethylic acid	$C_2H_3O,2SO_3,HO$
ic acid	$C_2H\ O_3,HO$
oform	$C_2H\ Cl_3$

OXIDE OF METHYL; PYROXYLIC SPIRIT; WOOD-SPIRIT; MeO,HO. wood-vinegar probably contains about $\frac{1}{100}$ part of this sub- h is separated from the great bulk of the liquid by subjecting distillation, and collecting apart the first portions which pass acid solution thus obtained is neutralized by hydrate of lime, the separated from the oil which floats on the surface, and from the the bottom of the vessel, and again distilled. A volatile liquid, like weak alcohol, is obtained; this may be strengthened in the r as ordinary spirit, by rectification, and ultimately rendered hydrous, by careful distillation from quick-lime by the heat of a Pure wood-spirit is a colourless, thin liquid, of peculiar odour, nt from that of alcohol, and burning, disagreeable taste; it boils

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[1] , wine, and ὕλη, wood; the termination ὕλη, or yl, is very frequently he sense of matter, material.

at 152° (66°·6C), and has a density of 0·798 at 68° (20C). The density of its vapour is 1·12. Wood-spirit mixes in all proportions with water, when pure; it dissolves resins and volatile oils as freely as alcohol, and is often substituted for alcohol in various processes in the arts, for which purpose it is prepared on a large scale. It may be burned instead of ordinary spirit in lamps; the flame is pale-coloured, like that of alcohol, and deposits no soot. Wood-spirit dissolves caustic baryta; the solution deposits, by evaporation *in vacuo*, acicular crystals, containing $BaO + MeO,HO$. Like alcohol, it dissolves chloride of calcium in large quantity, and gives rise to a crystalline compound, resembling that formed by alcohol, and containing, according to Kane, $CaCl + 2(MeO,HO)$.

Oxide of methyl; wood-ether; MeO. — One part of wood-spirit and 4 parts of concentrated sulphuric acid are mixed and exposed to heat in a flask fitted with a perforated cork and bent tube; the liquid slowly blackens, and emits large quantities of gas, which may be passed through a little strong solution of caustic potassa, and collected over mercury. This is the *wood-spirit ether*, a permanently gaseous substance, which does not liquefy at the temperature of 3° (— 16°·1C). It is colourless, has an ethereal odour, and burns with a pale and feebly luminous flame. Its specific gravity is 1·617. Cold water dissolves about 36 times its volume of this gas, acquiring thereby the characteristic taste and odour of the substance; when boiled, the gas is again liberated. Alcohol, wood-spirit, and concentrated sulphuric acid, dissolve it in still larger quantity.

Under the head of *ether* it has been mentioned that the generally received relation of this substance to the other ethyl-compounds had been rendered doubtful by recent researches. The same remark of course applies to methylic ether, which is in every respect analogous to common ethers. It was first proposed by Berzelius, and has long been urged by MM. Laurent and Gerhardt, that the composition of alcohol being expressed by the formula $C_4H_6O_2$, the true formula of ether was $C_8H_{10}O_2$, and not C_4H_5O. The correctness of this view has lately been established by a series of beautiful experiments carried out by Prof. Williamson. He found that the substance produced by dissolving potassium in alcohol, which has the formula C_4H_5O, KO, when acted upon by iodide of ethyl, furnishes iodide of potassium and perfectly pure ether. This reaction may be expressed by the two following equations:—

$$C_4H_5O,KO + C_4H_5I = KI + 2C_4H_5O, \text{ or}$$
$$C_4H_5O,KO + C_4H_5I = KI + C_8H_{10}O_2.$$

That in this reaction, not two equivalents of ether, as represented in the first equation, but a compound $C_8H_{10}O_2$ is formed, as expressed in the second, is clearly proved by substituting, when acting upon the compound C_4H_5O,KO, for the iodide of ethyl, the corresponding methyl-compound. In this case neither common ether nor methyl-ether is formed, but an intermediate compound $C_6H_8O_2 = C_4H_5O,C_2H_3O$. This substance is insoluble in water, and has a peculiar odour similar to that of ether, but boils at 50° (10°C).

It is very probable that the substances, which have been described by the terms ethyl and methyl, likewise are not C_4H_5 and C_2H_3, but C_8H_{10} and C_4H_6. The limits of this elementary work will not permit us to enter into the details of this question, which is still under the discussion of scientific chemists.

Chloride of methyl, MeCl. — This compound is most easily prepared by heating a mixture of 2 parts of common salt, 1 of wood-spirit, and 3 of concentrated sulphuric acid; it is a gaseous body, which may be conveniently collected over water, as it is but slightly soluble in that liquid. Chloride of methyl is colourless; it has a peculiar odour and sweetish taste, and burns

hen kindled, with a pale flame, greenish towards the edges, like most com-
astible chlorine-compounds. It has a density of 1·731, and is not liquefied
: 0° (—17°·7C). The gas is decomposed by transmission through a red-hot
ibe, with slight deposition of carbon, into hydrochloric acid gas and a car-
netted hydrogen, which has been but little examined.

Iodide of methyl, MeI, is a colourless and feebly combustible liquid,
btained by distilling together 1 part of phosphorus, 8 of iodine, and 12 or
i of wood-spirit. It is insoluble in water, has a density of 2·257, and
ils at 111° (43°·8C). The density of its vapour is 4·883. The action of
nc upon iodide of methyl in sealed tubes furnishes a colourless gas, appa-
ntly a mixture of several substances, among which methyl may occur.[1]
he residue contains iodide of zinc together with a volatile substance of very
sagreeable odour, which absorbs oxygen with so much avidity, that it takes
re when coming in contact with the air. It is zinc-methyl, C_4H_6Zn, cor-
sponding to zinc-ethyl. (See page 368.) When mixed with water it yields
xide of zinc and light carbonetted hydrogen.

Cyanide of methyl, MeCy. — If a dry mixture of sulphomethylate of
aryta and cyanide of potassium are heated in a retort, a very volatile liquid
f a powerful odour distils over. It generally contains hydrocyanic acid and
ater, from which it is separated by distillation, first over red oxide of mer-
ury, and then over anhydrous phosphoric acid. When thus purified, it has
n agreeable aromatic odour, and boils at 170°·6 (77°C). When boiled with
otassa, it undergoes a decomposition analogous to that of cyanide of ethyl,
see page 354); it absorbs 4 eq. of water, and yields acetic acid and am-
nonia.

$$\begin{array}{ll|ll} \text{MeCy} = & C_4H_3N & C_4H_3O,HO = & C_4H_4\ \ O_4 \\ & H_4\ \ O_4 & & H_3N \\ \hline & C_4H_7NO_4 & & C_4H_7NO_4 \end{array}$$

It has been mentioned that this compound may be obtained by abstracting
4 eq. of water from acetate of ammonia by means of phosphoric acid. (See
page 373.)

Compounds of methyl with bromine, fluorine, and sulphur have also been
obtained.

Sulphate of oxide of methyl, MeO,SO_3. — This interesting substance is
repared by distilling 1 part of wood-spirit with 8 or 10 of strong oil of
itriol: the distillation may be carried nearly to dryness. The oleaginous
quid found in the receiver is agitated with water, and purified by rectifica-
on from powdered caustic baryta. The product, which is the body sought,
a colourless oily liquid, of alliaceous odour, having a density of 1·324, and
oiling at 370° (187°7C). It is neutral to test-paper, and insoluble in water,
ut decomposed by that liquid, slowly in the cold, rapidly and with violence
a boiling temperature, into *sulphomethylic acid* and wood-spirit, which is
us reproduced by hydration of the liberated methylic ether. Anhydrous
me or baryta have no action on this summit; their hydrates, however, and
ose of potassa and soda, decompose it instantly, with production of a sul
homethylate of the base, and wood-spirit. When neutral sulphate of methyl
heated with common salt, it yields sulphate of soda and chloride of methyl;
ith cyanide of mercury or potassium, it gives a sulphate of the base, and
yanide of methyl; with dry formate of soda, sulphate of soda and formate
f methyl. These reactions possess great interest.

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[1] The same compound is believed to occur among the substances produced by the action of
galvanic current *upon acetic acid*. See valerianic acid, page 392.

NITRATE OF OXIDE OF METHYL, MeO,NO_5. — One part of nitrate of potassa is introduced into a retort, connected with a tubulated receiver, to which is attached a bottle, containing salt and water, cooled by a freezing mixture; a second tube serves to carry off the incondensible gases to a chimney. A mixture of one part of wood-spirit and 2 of oil of vitriol is made, and immediately poured upon the nitre; reaction commences at once, and requires but little aid from external heat. A small quantity of red vapour is seen to arise, and an ethereal liquid condenses, in great abundance, in the receiver and also in the bottle. When the process is at an end, the distilled products are mixed, and the heavy oily liquid obtained separated from the water. It is purified by several successive distillations by the heat of a water-bath from a mixture of chloride of calcium and litharge, and, lastly, rectified alone in a retort, furnished with a thermometer passing through the tubulature. The liquor begins to boil at about 140° (60°C); the temperature soon rises to 150° (65°·5C), at which point it remains constant; the product is then collected apart, the first and most volatile portions being contaminated with hydrocyanic acid and other impurities. Even with these precautions, the nitrate of methyl is not quite pure, as the analytical results show. The properties of the substance, however, remove any doubts respecting its real nature.

Nitrate of methyl is colourless, neutral, and of feeble odour; its density is 1·182; it boils at 150° (65°·5C), and burns, when kindled, with a yellow flame. Its vapour has a density of 2·64, and is eminently explosive; when heated in a flask or globe to 300° (140°C), or a little above, it explodes with fearful violence; the determination of the density of the vapour is, consequently, an operation of danger. Nitrate of methyl is decomposed by a solution of caustic potassa into nitrate of that base and wood-spirit.

OXALATE OF OXIDE OF METHYL, MeO, C_2O_3. — This beautiful and interesting substance is easily prepared by distilling a mixture of equal weights of oxalic acid, wood-spirit, and oil of vitriol. A spirituous liquid collects in the receiver, which, exposed to the air, quickly evaporates, leaving the oxalic methyl-ether in the form of rhombic transparent crystalline plates, which may be purified by pressure between folds of bibulous paper, and re-distilled from a litlle oxide of lead. The product is colourless, and has the odour of common oxalic ether; it melts at 124° (51°·1C), and boils at 322° (161°C). It dissolves freely in alcohol and wood-spirit, and also in water, which, however, rapidly decomposes it, especially when hot, into oxalic acid and wood-spirit. The alkaline hydrates effect the same change even more easily. Solution of ammonia converts it into oxanide and wood-spirit. With dry ammoniacal gas it yields a white, solid substance, which crystallizes from alcohol in pearly cubes; this new body, designated *oxamethylane*, or oxamate of methyl, contains $C_6H_5NO_6{=}C_2H_3O,C_4H_2NO_5$.

Many other salts of oxide of methyl have been formed and examined. The *acetate*, $MeO,C_4H_3O_3$, is abundantly obtained by distilling 2 parts of wood-spirit with 1 of crystallizable acetic acid, and 1 of oil of vitriol. It much resembles acetic ether, having a density of 0·919, and boiling at 136° (57°·8C); the density of its vapour is 2·563. This compound is isomeric with formic ether. *Formate of methyl*, MeO,C_2HO_3, is prepared by heating in a retort equal weights of sulphate of methyl and dry formate of soda, it is very volatile, lighter than water, and is isomeric with hydrate of acetic acid. *Chlorocarbonic methyl-ether* is produced by the action of that gas upon wood-spirit; it is a colourless, thin, heavy, and very volatile liquid, containing $C_4H_3ClO_4$ $=C_2H_3O,C_2ClO_3$. It yields with dry ammonia a solid crystallizable substance, called *urethylane*, $C_4H_5NO_4$. (See page 358.)

SULPHOMETHYLIC ACID, $MeO,2SO_3,HO$. — Sulphomethylate of baryta is prepared in the same manner as the sulphovinate; 1 part of wood-spirit is

owly mixed with 2 parts of concentrated sulphuric acid, the whole heated ebullition, and left to cool, after which it is diluted with water and neualized with carbonate of baryta. The solution is filtered from the insoble sulphate, and evaporated, first in a water-bath, and afterwards *in vacuo* the due degree of concentration. The salt crystallizes in beautiful square lourless tables, containing $BaO,C_2H_3O,2SO_3+2HO$, which effloresce in dry r, and are very soluble in water. By exactly precipitating the base from is substance by dilute sulphuric acid, and leaving the filtered liquid to evarate in the air, hydrated sulphomethylic acid may be procured in the form a sour, syrupy liquid, or as minute acicular crystals, very soluble in ater and alcohol. It is very instable, being decomposed by heat in the me manner as sulphovinic acid. *Sulphomethylate of potassa* crystallizes in nall, nacreous, rhombic tables, which are deliquescent; it contains KO, $H_3O,2SO_3$. The lead-salt is also very soluble.

FORMIC ACID.—As alcohol by oxidation under the influence of finely-divided latinum gives rise to acetic acid, so wood-spirit, under similar circumstans, yields a peculiar acid product, produced by the substitution of 2 eq. of xygen for 2 eq. of hydrogen, to which the term *formic* is given, from its ocurrence in the animal kingdom, in the bodies of ants. The experiment ay be easily made by inclosing wood-spirit in a glass jar with a quantity f platinum-black, and allowing moderate excess of air; the spirit is graually converted into formic acid. There has not been found an intermeate product corresponding to aldehyde. Anhydrous formic acid, as in the lts, contains C_2HO_3, or the elements of 2 eq. carbonic oxide, and 1 eq. water.

Pure hydrate formic acid, C_2HO_3,HO, is obtained by the action of sulphuretted hydrogen on dry formate of lead. The salt, reduced to fine powder, is very gently heated in a glass tube connected with a condensing apparatus, through which a current of dry sulphuretted hydrogen gas is transmitted. It forms a clear, colourless liquid, which fumes slightly in the air, of exceedgly penetrating odour, boiling at 209° (98°·5C), and crystallizing in large rilliant plates when cooled below 32° (0°C). The sp. gr. of the acid is 1·235; it mixes with water in all proportions; the vapour is inflammable, d burns with a blue flame. A second hydrate, containing 2 eq. of water, xists; its density is 1·11, and it boils at 223° (106°·1C). In its concentrated form this acid is extremely corrosive; it attacks the skin, forming a blister or an ulcer, painful and difficult to heal. A more dilute acid may be repared by a variety of processes: starch, sugar, and many other organic ubstances often yield formic acid when heated with oxidizing agents; a convenient method is the following:—1 part of sugar, 3 of binoxide of manganese, and 2 of water, are mixed in a very capacious retort, or large metal still; 3 parts of oil of vitriol, diluted with an equal weight of water, are hen added, and when the first violent effervescence from the disengagement f carbonic acid has subsided, heat is cautiously applied, and a considerable uantity of liquid distilled over. This is very impure; it contains a volale oily matter, and some substance which communicates a pungency not roper to formic acid in that dilute state. The acid liquid is neutralized ith carbonate of soda, and the resulting formate purified by crystallization, d if needful, by animal charcoal. From this, or any other of its salts, lution of formic acid may be readily obtained by distillation with dilute lphuric acid. It has an odour and taste much resembling those of acetic id, reddens litmus strongly, and decomposes the alkaline carbonates with fervescence.

Another process for making formic acid consists in distilling dry oxalic id, mixed with its own weight of sand or pumice-stone in a glass retort. rbonic oxide and carbonic acid are disengaged, while a very acid liquid stils, which is formic acid contaminated with a small quantity of oxalic

acid. By redistilling this mixture pure distilled formic acid is obtained. This process yields a very strong acid, but only a small quantity in proportion to the oxalic acid employed.

Formic acid, in quantity, may be extracted from ants by distilling the insects with water, or by simply macerating them in the cold liquid.

Formic acid is readily distinguished from acetic acid by heating it with a little solution of oxide of silver or mercury; the metal is reduced, and precipitated in a pulverulent state, while carbonic acid is extricated, this reaction is sufficiently intelligible. The protochloride of mercury is reduced by the aid of the elements of water, to calomel, carbonic acid and hydrochloric acids being formed.

The most important salts of formic acid are the following: — *Formate of soda* crystallizes in rhombic prisms containing 2 eq. of water; it is very soluble, and is decomposed like the rest of the salts by hot oil of vitriol with evolution of pure carbonic oxide. Fused with many metallic oxides, it causes their reduction. *Formate of potassa* is with difficulty made to crystallize from its great solubility. *Formate of ammonia* crystallizes in square prisms; it is very soluble, and is decomposed by a high temperature into hydrocyanic acid and water, the elements of which it contains, $NH_4O,C_2HO_3 - 4HO = C_2NH$. This decomposition is perfectly analogous to that of acetate of ammonia, see page 272. The salts of *baryta*, *strontia*, *lime*, and *magnesia* form small prismatic crystals, soluble without difficulty. *Formate of lead* crystallizes in small, diverging, colourless needles, which require for solution 40 parts of cold water. The formates of *manganese*, *protoxide of iron*, *zinc*, *nickel*, and *cobalt*, are also crystallizable. That of *copper* is very beautiful, constituting bright blue, rhombic prisms of considerable magnitude. *Formate of silver* is white, but slightly soluble, and decomposed by the least elevation of temperature.

Chloroform.—This substance is produced, as already remarked, when an aqueous solution of caustic alkali is made to act upon chloral. It may be obtained with greater facility by distilling alcohol, wood-spirit, or acetone with a solution of chloride of lime. 1 part of hydrate of lime is suspended in 24 parts of cold water, and chlorine passed through the mixture until nearly the whole lime is dissolved. A little more hydrate is then added to restore the alkaline reaction, the clear liquid mixed with 1 part of alcohol or wood-spirit, and, after an interval of 24 hours, cautiously distilled in a very spacious vessel. A watery liquid containing a little spirit and a heavy oil collect in the receiver: the latter, which is the chloroform, is agitated with water, digested with chloride of calcium, and rectified in a water-bath. It is a thin, colourless liquid of agreeable ethereal odour, much resembling that of Dutch-liquid, and sweetish taste. Its density is 1·48, and it boils at 141°·8 (61°C); the density of its vapour is 4·116. Chloroform is with difficulty kindled, and burns with a greenish flame. It is nearly insoluble in water, and is not affected by concentrated sulphuric acid. Alcoholic solution of potassa decomposes it with production of chloride of potassium and formate of potassa.

Chloroform may be prepared on a larger scale by cautiously distilling together good commercial chloride of lime, water and alcohol. The whole product distils over with the first portions of water, so that the operation may be soon interrupted with advantage.

This substance has been called strongly into notice from its remarkable effects upon the animal system in producing temporary insensibility to pain when its vapour is inhaled.

Chloroform contains C_2HCl_3; it is changed to formic acid by the substitution of three eq. of oxygen for the three eq. of chlorine removed by the alkaline metal.

Bromoform, C_2HBr_3, is a heavy, volatile liquid, prepared by a similar pro-ss, bromine being substituted in the place of chlorine. It is converted by kali into bromide of potassium and formate of potassa. *Iodoform*, C_2HI_3, a solid, yellow, crystallizable substance, easily obtained by adding alco-lic solution of potassa to tincture of iodine, avoiding excess, evaporating e whole to dryness, and treating the residue with water. Iodoform is early insoluble in water, but dissolves in alcohol, and is decomposed by al-alis in the same manner as the preceding compounds.

FORMOMETHYLAL.—This is a product of the distillation of wood-spirit with ilute sulphuric acid and binoxide of manganese. The distilled liquid is aturated with potassa, by which the new substance is separated as a light ily fluid. When purified by rectification, it is colourless, and of agreeable romatic odour; it has a density of 0·855, boils at 170° (41°C), and is com-letely soluble in three parts of water. It contains $C_6H_8O_4$. It corresponds o acetal, and may be viewed as a compound of 2 eq. of ether, with 1 eq. of the yet unknown aldehyde of the methyl-series, $C_6H_8O_4{=}2C_2H_3O,C_2H_2O_2$.

METHYL-MERCAPTAN is prepared by a process similar to that recommended for ordinary mercaptan, sulphomethylate of potassa being substituted for the sulphovinate of lime. It is a colourless liquid, of powerful alliaceous odour, and lighter than water; it boils at 68° (20°C), and resembles mer-captan in its action on red oxide of mercury.

PRODUCTS OF THE ACTION OF CHLORINE ON THE COMPOUNDS OF METHYL.—Chlorine acts upon the methylic compounds in a manner strictly in obedi-ence to the law of substitution: the carbon invariably remains intact, and every proportion of hydrogen removed is replaced by an equivalent quantity of chlorine. Methylic ether and chlorine, in a dry and pure condition, yield a volatile liquid product, containing C_2H_2ClO: the experiment is at-tended with great danger, as the least elevation of temperature gives rise to a violent explosion. This product in its turn furnishes, by the continued action of the gas, a second liquid, containing C_2HCl_2O. The whole of the hydrogen is eventually lost, and a third compound, C_2Cl_3O, produced.

Chloride of methyl, C_2H_3Cl, in like manner gives rise to three successive products. The first, $C_2H_2Cl_2$, is a new volatile liquid, much resembling chloride of olefiant gas; the second, C_2HCl_3, is no other than chloroform; the third is bichloride of carbon, C_2Cl_4.

Some of these substances, especially chloroform and bichloride of carbon, have been obtained also by the action of chlorine on light carbonetted hy-drogen (marsh-gas), which thus becomes connected with the methyl-series. It may be regarded as hydride of methyl, a view which is likewise sup-ported by its formation from zinc-methyl (see page 382); thus we have the following series.

Hydride of methyl	C_2H_3H.	Light carbonetted hydrogen.
Chloride of methyl	C_2H_3Cl.	
Chlorinetted chloride of methyl	$C_2H_2Cl_2$.	
Bichlorinetted " "	C_2HCl_3.	Chloroform.
Trichlorinetted " "	C_2Cl_4.	Bichloride of carbon.

The acetate of methyl, $C_6H_6O_4$, gives $C_6H_4Cl_2O_4$, and $C_6H_3Cl_3O_4$; the other methyl-ethers are without doubt affected in a similar manner.

Commercial wood-spirit is very frequently contaminated with other sub-stances, some of which are with great difficulty separated. It sometimes contains aldehyde, often acetone and propione, and very frequently a vola-le oil, which is precipitated by the addition of water, rendering the whole urbid. The latter is a mixture of several hydrocarbons, very analogous to those contained *in coal-tar*. A specimen of wood-spirit, from Wattwyl, in Switzerland, was found by Gmelin to contain a volatile liquid, differing in

bonic acids, together with carbonate of amyl ($AylO,C_2ClO_3+HO=AylO,CO_2+HCl+CO_2$). Carbonate of amyl is a colourless liquid of an aromatic odour, boiling at 438°·8 (226°C). Alcoholic solution of potassa converts this ether into fusel-oil, carbonate of potassa being formed at the same time.

Sulphide of amyl, *amyl-mercaptan*, and numerous other compounds of like nature, have been described.

SULPHAMYLIC ACID.—When equal weights of potato-oil and strong sulphuric acid are mixed, heat is evolved, accompanied by blackening and partial decomposition. The mixture diluted with water, and saturated with carbonate of baryta, affords sulphate of that base, and a soluble salt corresponding to the sulphovinate. The latter may be obtained in a crystalline state by gentle evaporation, and purified by re-solution and the use of animal charcoal. It forms small, brilliant, pearly plates, very soluble in water and alcohol, containing $BaO,C_{10}H_{11}O,2SO_3+HO$. The baryta may be precipitated from the salt by dilute sulphuric acid, and the hydrated sulphamylic acid concentrated by spontaneous evaporation to a syrupy, or even crystalline state; it has an acid and bitter taste, strongly reddens litmus-paper, and is decomposed by ebullition into potato-oil and sulphuric acid. The potassa-salt forms groups of small radiated needles, very soluble in water. The sulphamylates of lime and protoxide of lead are also soluble and crystallizable.

AMYLENE.—By the distillation of potato-oil with anhydrous phosphoric acid, a volatile, colourless, oily liquid is procured, quite different in properties from the original substance. It is lighter than water, boils at 102°·2 (39°C), and contains no oxygen. Its composition is represented by the formula $C_{10}H_{10}$; consequently it not only corresponds to the olefiant gas in the alcohol-series, but is isomeric with that substance. Like olefiant gas it combines directly with chlorine and bromine, giving rise to compounds $C_{10}H_{10}Cl_2$ and $C_{10}H_{10}Br_2$. The vapour, however, has a density of 2·68, which is $2\frac{1}{2}$ times that of olefiant gas, every measure containing 5 measures of hydrogen.

Together with this substance several other hydrocarbons are formed, especially the one to which the name *paramylene* has been given. It contains $C_{20}H_{20}$, and boils at 320° (160°C).

VALERIANIC OR VALERIC ACID.—M. Dumas has shown that when a mixture of equal parts of quicklime and hydrate of potassa is moistened with alcohol, and the whole subjected to a gentle heat, out of contact of air, the alcohol is oxidized to acetic acid, with evolution of pure hydrogen gas. At a higher temperature the acetate of potassa produced is in turn decomposed, yielding carbonate of potassa and light carbonetted hydrogen. Wood-spirit, by similar treatment, yields hydrogen and formate of potassa, which, as the heat increases, becomes converted into carbonate, with continued disengagement of hydrogen. In like manner potato-oil, the third alcohol, suffers under similar circumstances, conversion into a new acid, bearing to it the same relation that acetic acid does to common alcohol, and formic acid to wood-spirit, hydrogen being at the same time evolved. The body thus produced is found to be identical with a volatile oily acid distilled from the root *Valeriana officinalis*.

In preparing artificial valerianic acid, the potato-oil is heated in a flask with about ten times its weight of the above-mentioned alkaline mixture during the space of 10 or 12 hours; the heat is applied by a bath of oil or fusible-metal raised to the temperature of 390° (198°·8C) or 400° (204°·4C). When cold, the nearly white solid residue is mixed with water, excess of sulphuric or phosphoric acid added, and the whole subjected to [illegible]tion. The distilled liquid is supersaturated with potassa, evaporated [illegible]ryness to dissipate any undecomposed potato-oil, and then mixed

with somewhat diluted sulphuric acid in excess. The greater part of the valerianic acid then separates as an oily liquid, lighter than water; this is a terhydrate of the acid, containing three equivalents of water, one of which is basic. When this hydrate is distilled alone, it undergoes decomposition; water, with a little of the acid, first appears, and eventually the pure acid, in the form of a thin, fluid, colourless oil, of the persistent and characteristic odour of valerian-root. It has a sharp and acid taste, reddens litmus strongly, bleaches the tongue, and burns when inflamed with a bright, yet smoky light. Valerianic acid has a density of 0·937; it boils at 370° (175°C). Placed in contact with water, it absorbs a certain quantity, and is itself to a certain extent soluble. The salts of this acid present but little interest, as few among them seem to be susceptible of crystallizing. The liquid acid is found by analysis to contain $C_{10}H_9O_3,HO$, and the silver-salt, $AgO,C_{10}H_9O_3$. The ether-compound of valerianic acid has been already mentioned (page 357). By treatment with ammonia this ether is converted into *valeramide* $C_{10}H_{11}NO_2{=}C_{10}H_9O_2,NH_2$, (analogous to acetamide,) which, under the influence of anhydrous phosphoric acid loses 2 more eq. of water, becoming valeronitrile $C_{10}H_9N{=}C_8H_9,C_2N$ or cyanide of butyl. The former is a fusible crystalline substance, the latter a volatile liquid, having a boiling point of 257° (125°C). It was first obtained by the action of oxydizing agents upon gelatin. (See Section VIII on the components of the animal body.)

A more advantageous mode of preparing valerianic acid is the following: —4 parts of bichromate of potassa in powder, 6 parts of oil of vitriol, and 8 parts of water are mixed in a capacious retort; 1 part of pure potato-oil is then added by small portions, with strong agitation, the retort being plunged into cold water to moderate the violence of the reaction. When the change appears complete, the deep green liquid is distilled nearly to dryness, the product mixed with excess of caustic potassa, and the aqueous solution separated mechanically from a pungent, colourless, oily liquid, which floats upon it, and which is valerianate of amyl. The alkaline solution is then evaporated to a small bulk and decomposed by sulphuric acid as already directed.

Valerianic acid is found in *angelica root*, in the bark of *Viburnum opulus*, and probably exists in many other plants; it is generated by the spontaneous decomposition of azotized substances, mineral and vegetable, and is produced in many chemical reactions in which oxidizing agents are employed.

If an open jar be set in a plate containing a little water, and having beneath it a capsule with heated platinum-black, upon which potato-oil is slowly dropped in such quantity as to be absorbed by the powder, the sides of the jar become speedily moistened with an acid liquid, which collects in the plate, and may be easily examined. This liquid, saturated with baryta-water, evaporated to dryness, and the product distilled with solution of phosphoric acid, yields valerianic acid.[1]

Some very beautiful, and for the progress of organic chemistry, highly important results, have lately been obtained by the action of electricity upon valerianic acid. By submitting a solution of valerianate of potassa to a galvanic current, produced by 4 elements of Bunsen's battery, Dr. Kolbe observed that potassa and pure hydrogen were evolved at the negative pole, while at the positive pole valerianic and carbonic acids, an odorous inflammable gas, and an ethereal liquid, made their appearance. The inflammable gas obtained in this reaction is a carbohydrogen C_8H_8 which had been pre-

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[1] Anhydrous valerianic acid is formed by the reaction between valerianate of potassa and oxychloride of phosphorus,

$$5(KO,\ C_{10}H_9O_3)\ \text{and}\ PCl_3O_2{=}2KOPO_5,\ \text{and}\ 3KCl,\ \text{and}\ 5(C_{10}H_9O_3).$$

It is an oleaginous liquid lighter than water. Boiling water changes it slowly into the hydrated acid, while this transformation is rapidly affected by solutions of the alkalies. It boils at 419° (215°C), and distils unchanged.—R. B.

viously isolated by Mr. Faraday from the oily products separated from compressed oil gas. This substance, to which the name *butylene* has been given, is perfectly analogous to the olefiant gas (ethylene), propylene and amylene which have been previously described. It combines with chlorine and bromine, forming substances analogous to Dutch liquid. The oily liquid formed together with amylene, in the electrolysis of valerianic acid, is a mixture of several substances, among which a hydrocarbon, of the remarkable composition C_8H_9, predominates. This body, to which the name *butyl* or *valyl* has been given, is a colourless liquid, of an agreeable ethereal odour, and boils at 226°·4 (108°C). Kolbe believes that this hydrocarbon must be viewed as a compound analogous to methyl, ethyl, and amyl, with which we have become acquainted, and that it forms the radical of an alcohol yet to be discovered, having the formula C_8H_9O,HO and analogous to methyl-, ethyl-, and amyl-alcohols, an alcohol which, by oxidation, would yield the acid $C_8H_7O_3$, HO, i. e., butyric acid, just as the three alcohols mentioned are converted respectively into formic, acetic, and valeric acids. Kolbe considers butyl to be one of the proximate constituents of valeric acid, which he views as an intimate combination of butyl with oxalic acid, butyl-oxalic acid $C_{10}H_9O_3,HO$ $=C_8H_9,C_2O_3HO$. According to this view, the transformation of valeric acid under the influence of the galvanic current is readily explained. The oxygen evolved at the positive pole by the electrolysis of water oxidizes the oxalic to carbonic acid, and liberates the butyl, portions of which are farther attacked by the oxygen, and deprived of 1 eq. of hydrogen, thus giving rise to the simultaneous evolution of butylene. If this view holds good for butyric acid, it must be equally true of propionic, acetic, and formic acid, and of a great number of analogous acids, which will be described in the subsequent chapters of this Manual.

Propionic acid will be ethyl-oxalic acid, acetic acid methyl-oxalic, and lastly, formic acid hydrogen-oxalic acid, thus—

Formic acid...........................	$C_2\ HO_3,\ HO=\ \ H\ ,C_2O_3,HO$
Acetic acid...........................	$C_4\ H_3O_3,HO=C_2H_3,C_2O_3,HO$
Propionic acid...........................	$C_6\ H_5O_3,HO=C_4H_5,C_2O_3,HO$
Valeric acid	$C_{10}H_9O_3,HO=C_8H_9,C_2O_3,HO$ [1]

This view is borne out by the electrolytic decomposition of acetic acid, which yields a gas, considered by Kolbe to be methyl. Several collateral facts have furnished additional support to this theory, amongst which may be quoted the remarkable deportment of the ammonia-salts of these acids under the influence of anhydrous phosphoric acid. In this reaction, oxalic, formic,

[1] Butyric acid constitutes the fifth member of this series as a combination of propyl with oxalic acid or propyl-oxalic acid,

Butyric acid.........................$C_8H_9O_3,HO=C_6H_7,C_2O_3,HO$

As valyl is formed from valeric acid, so the decomposition of butyric acid should yield propyl C_6H^7, the oxide of which C_6H_7O has been detected in cod-liver oil in combination with oleic and margaric acid.

Butylic alcohol of Wurtz appears to fill up this vacancy in the alcohol series. It was extracted from rectified potato-oil by fractional distillations, retaining that which passes between 226°·4 (103°) and 244°·4 (118°). By subsequent purification a liquid is obtained which boils at 233°·6 (112°), is lighter than water, has the odour of amylic alcohol, but less disagreeable. Fused potassa changes it into butyric acid with the liberation of hydrogen. Its composition is $C_8H_{10}O_2=C_8H^9O.HO$, or hydrate of oxide of valyl.

Butylic alcohol, when mixed with its own weight of strong sulphuric acid and after twenty-four hours' repose saturated with carbonate of potassa, yields sulphate and sulphobutylate of potassa. The latter dissolves readily in boiling absolute alcohol, from which it is deposited in anhydrous pearly crystals of the composition $KO,C_8H_9O.2SO_3$.

The cyanate and cyanurate of butylic ether yield with potassa a nitrogenous product, *butylamin*, $NH_2C_8H_9$, in the same way as the cyanates and cyanurates of ethyl, methyl, or *amyl*, *yield* respectively ethylamin, $NH_2C_4H_5$, methylamin $NH_2C_2H_3$, and amylamin NH_2 $C_{10}H_{11}$.—*R. B.*

etic, propionic, and valeric acids yield respectively cyanogen and the cyanides of hydrogen, methyl, ethyl, and butyl.

$$NH_4O, \quad C_2O_3 - 4HO = \quad C_2N$$
$$NH_4O, \ H, C_2O_3 - 4HO = \ H, C_2N$$
$$NH_4O, C_2H_3, C_2O_3 - 4HO = C_2H_3, C_2N$$
$$NH_4O, C_4H_5, C_2O_3 - 4HO = C_4H_5, C_2N$$
$$NH_4O, C_8H_9, C_2O_3 - 4HO = C_8H_9, C_2N$$

We have seen, moreover, that the cyanides of methyl and ethyl, when treated with the alkalis are readily reconverted into acetic and propionic acid, and in the Section on cyanogen it will be shown that this substance and hydrocyanic acid are indeed easily convertible into oxalate and formate of ammonia. All these facts are readily intelligible by the view proposed by Dr. Kolbe.

Chlorovalerisic acid.—When dry chlorine is passed for a long time into pure valerianic acid, in the dark, the gas is absorbed in great quantity, and much hydrochloric acid produced; towards the end of the operation a little heat becomes necessary. The product is a semi-fluid transparent substance, heavier than water, odourless, and of acrid burning taste. It does not congeal when exposed to a very low temperature, but acquires complete fluidity when heated to 86° (30°C). It cannot be distilled without decomposition. When put into water it forms a thin, fluid hydrate, which afterwards dissolves to a considerable extent. This body is freely soluble in alkalis, from which it is again precipitated by the addition of an acid. Chlorovalerisic acid contains $C_{10}(H_6Cl_3)O_3.HO$.

Chlorovalerosic acid.—This is the ultimate product of the action of chlorine on the preceding substance, aided by exposure to the sun. It resembles chlorovalerisic acid in appearance and properties, being semi-fluid and colourless, destitute of odour, of powerful pungent taste, and heavier than water. It can neither be solidified by cold, nor distilled without decomposition. In contact with water, it forms a hydrate containing 3 eq. of that substance, which is slightly soluble. In alcohol and ether it dissolves with facility. It forms salts with bases, of which the best defined is that of silver. Chlorovalerosic acid is composed of $C_{10}(H_5Cl_4)O_3,HO$.

Fusel-oil of grain-spirit.—The fusel-oil separated in large quantities from grain-spirit by the London rectifiers consists chiefly of potato-oil (hydrated oxide of amyl) mixed with alcohol and water. Sometimes it contains in addition more or less of the ethyl- or amyl-compounds of certain fatty acids thought to have been identified with œnanthic and margaric acids. These last-named substances form the principal part of the nearly solid fat produced in this manner in whisky-distilleries conducted on the old plan. Mulder has described, under the name of *corn-oil*, another constituent of the crude fusel-oil of Holland; it has a very powerful odour resembling that of some of the umbelliferous plants, and is unaffected by solution of caustic potassa. According to Mr. Rowney, the fusel-oil of the Scotch distilleries contains in addition a certain quantity of capric acid $C_{20}H_{20}O_4$ which is one of the constituents of butter.

The fusel-oil of *marc-brandy* of the south of France was found by M. Balard to contain potato-oil and œnanthic ether. Potato-oil has been separated from the spirit distilled from beet-molasses, and from artificial grape-sugar made by the aid of sulphuric acid. Although much obscurity yet hangs over the history of these substances, it is generally supposed that they are products of the fermentation of sugar, and have an origin contemporaneous with that of common alcohol.

It is *impossible to leave the* history of the alcohols without alluding to *some results of great* importance for the elucidation of organic compounds

generally, which the study of these substances has elicited. When describing the three alcohols, discussed in the preceding chapter, we have repeatedly pointed out the remarkable analogy presented by the properties and the general deportment of these three bodies. If we compare the composition of the three alcohols,

Methyl-alcohol	$C_2H_4O_2$
Ethyl-alcohol	$C_4H_6O_2$
Amyl-alcohol	$C_{10}H_{12}O_2$

we find that their formulæ present an unmistakable symmetry. All three contain the same amount of oxygen, only the carbon and hydrogen vary. This variation, however, takes place in very simple relations. Thus we find the difference of ethyl- and methyl-alcohol to be $C_4H_6O_2 - C_2H_4O_2 = C_2H_2$, the difference of amyl- and methyl-alcohol to be $C_{10}H_{12}O_2 - C_2H_4O_2 = C_8H_8 = 4C_2H_2$. The same elementary difference of course prevails likewise between all the derivatives of the three alcohols.

Iodide of methyl	C_2H_3I
Iodide of ethyl	$C_4H_5I = C_2H_3I + C_2H_2$
Iodide of amyl	$C_{10}H_{11}I = C_2H_3I + 4C_2H_2$

or

Formic acid	C_2HO_3,HO
Acetic acid	$C_4H_3O_3,HO = C_2HO_3,HO + C_2H_2$
Valeric acid	$C_{10}H_9O_3,HO = C_2HO_3,HO + 4C_2H_2$

Methylic, ethylic, and amylic alcohols are by no means the only members of this class which are known. In the succeeding sections of this work will be noticed a series of compounds evidently of a perfectly analogous character which have been discovered. By submitting castor-oil to a series of processes, M. Bouis has formed an alcohol, which has been called "caprylic alcohol." According to M. Dumas, spermaceti contains another analogous substance, cetylic alcohol, which is a solid: and Mr. Brodie has prepared two alcohols, cerotylic and mellisic, from ordinary bees' wax. The composition of these substances stands in exactly the same relation to that of the preceding alcohols, which we have pointed out, as will be seen from the following table:—

Caprylic alcohol	$C_{16}H_{18}O_2 = C_2H_4O_2 + 7C_2H_2$
Cetylic alcohol	$C_{32}H_{34}O_2 = C_2H_4O_2 + 15C_2H_2$
Cerotylic alcohol	$C_{54}H_{56}O_2 = C_2H_4O_2 + 26C_2H_2$
Melissic alcohol	$C_{60}H_{62}O_2 = C_2H_4O_2 + 29C_2H_2$

These four alcohols, when submitted to the action of oxidizing agents, are converted into four acids, analogous to formic and acetic acid, and which stand to each other, and to formic and acetic acid, in exactly the same relation as the various alcohols.

Caprylic acid	$C_{16}H_{15}O_3,HO = C_2HO_3,HO + 7C_2H_2$
Cetylic acid	$C_{32}H_{31}O_3,HO = C_2HO_3,HO + 15C_2H_2$
Cerotylic acid	$C_{54}H_{53}O_3,HO = C_2HO_3,HO + 26C_2H_2$
Melissic acid	$C_{60}H_{59}O_3,HO = C_2HO_3,HO + 29C_2H_2$

A glance at these tables shows that all the alcohols known differ from methyl-alcohols by C_2H_2, or a multiple of it. At the same time, it is evident that the series by no means regularly ascends. Thus we perceive that between ethylic and amylic alcohols two compounds are possible; in like manner two between amylic and caprylic alcohols.

Even now the parallel series of volatile acids is far more complete than

ɜ alcohols. At present the following members of this group are
ıich are placed in juxtaposition with the collateral alcohols:—

ŋl-alcohol.........	$C_2 H_4 O_2$	Formic acid	$C_2 H_2 O_4$
-alcohol	$C_4 H_6 O_2$	Acetic acid	$C_4 H_4 O_4$
ŋl-alcohol)........	$C_6 H_8 O_2$	Propionic acid.........	$C_6 H_6 O_4$
l-alcohol).........	$C_8 H_{10} O_2$	Butyric acid............	$C_8 H_8 O_4$
·alcohol	$C_{10} H_{12} O_2$	Valeric acid............	$C_{10} H_{10} O_4$
	$C_{12} H_{14} O_2$	Caproic acid............	$C_{12} H_{12} O_4$
	$C_{14} H_{16} O_2$	Œnanthylic acid	$C_{14} H_{14} O_4$
l-alcohol	$C_{16} H_{18} O_2$	Caprylic acid	$C_{16} H_{16} O_4$
	$C_{18} H_{20} O_2$	Pelargonic acid	$C_{18} H_{18} O_4$
	$C_{20} H_{22} O_2$	Capric acid.............	$C_{20} H_{20} O_4$
&c.	&c.	&c.	&c.

ıt continue the series of acids uninterruptedly to $C_{38}H_{38}O_4$ (balenic
with intervals even much higher up to acids containing 54 and
equivalents of carbon. Most of the acids belonging to this series
separated from fats, and hence this series is frequently designated
ne of the series of *fatty acids*.

of analogous substances whose composition varies by C_2H_2, or a
f it, is called a series of *homologous* bodies—a name first used by
dt, to whom we are much indebted for the elucidation of this sub-
ɜ evident that there exist as many such homologous series as there
tives of any one of the alcohols. We may construct a series of
ıs radicals, or ethers, or hydrocarbons.

ŋl	$C_2 H_3$	Methyl-ether..	$C_2 H_3 O$		$C_2 H_2$
....	$C_4 H_5$	Ether	$C_4 H_5 O$	Ethylene......	$C_4 H_4$
·l ?	$C_6 H_7$	(Tetryl-ether).	$C_6 H_7 O$	Propylene	$C_6 H_6$
....	$C_8 H_9$		$C_8 H_9 O$	Butylene......	$C_8 H_8$
....	$C_{10} H_{11}$	Amyl-ether....	$C_{10} H_{11} O$	Amylene	$C_{10} H_{10}$
ıyl	$C_{12} H_{13}$		$C_{12} H_{13} O$	Caproylene...	$C_{12} H_{12}$
	$C_{14} H_{15}$		$C_{14} H_{15} O$		$C_{14} H_{14}$
	$C_{16} H_{17}$		$C_{16} H_{17} O$	Caprylene	$C_{16} H_{16}$

e series of homologous bodies still present numerous gaps; none
ıore than that of the alcohols which may be taken as the prototype
rest; but since the existence of these homologous series was first
ıt, many gaps have been filled, and it may be expected that before
apid strides of organic chemistry will render them complete.

ıperties of the various members belonging to homologous series
change as we ascend in the series. The most characteristic alte-
the diminution of volatility. A regular difference between the
ints of homologous substances was first pointed out by H. Kopp.
mple may be taken the series of fatty acids:—

		Boiling points. F.	C.	Differences. F.	C.
ic acid..........	$C_2 H_2 O_4$	209°	98°·5		
				37°	20°·5
ɜ acid	$C_4 H_4 O_4$	246°	119°		
				38°	21°
ɔnic acid	$C_6 H_6 O_4$	284°	140°		
				30°	17°
ic acid	$C_8 H_8 O_4$	314°·6	157°		
				33°·4	18°
ic acid..........	$C_{10} H_{10} O_4$	347°	175°		
				41°·4	23°
ic acid	$C_{12} H_{12} O_4$	388°·4	198°		

is table it is evident that the boiling temperature of the homolo-
rises on an *average* 36°·3 (19°·9C) for every increment of C_2H_2
egular difference has been observed in the boiling points of many

homologous compounds. As yet, however, the number of cases in which discrepancies occur is very considerable.

The substances discussed in the next three sections have but little relation to the alcohols; they may, however, be here most conveniently described.

BITTER-ALMOND OIL AND ITS PRODUCTS.

The volatile oil of bitter almonds possesses a very high degree of interest, from its study having, in the hands of MM. Liebig and Wöhler, led to the first discovery of a compound organic body capable of entering into direct combination with elementary principles, as hydrogen, chlorine, and oxygen, and playing in some degree the part of a metal. The oil is supposed to be the hybride of a salt-basyle, containing $C_{14}H_5O_2$, called *benzoyl*, from its relation to benzoic acid, which radical is to be traced throughout the whole series; it has been isolated, and will be described among the products of distillation of the benzoates.

Table of Benzoyl-Compounds.

Benzoyl, symbol Bz	$C_{14}H_5O_2$
Hydride of benzoyl; bitter-almond oil	$C_{14}H_5O_2H$
Hydrated oxide of benzoyl; benzoic acid	$C_{14}H_5O_2O,HO$
Chloride of benzoyl	$C_{14}H_5O_2Cl$
Bromide of benzoyl	$C_{14}H_5O_2Br$
Iodide of benzoyl	$C_{14}H_5O_2I$
Sulphide of benzoyl	$C_{14}H_5O_2S$.

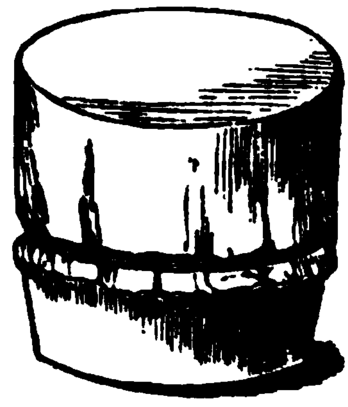
HYDRIDE OF BENZOYL; BITTER-ALMOND OIL; BzH.—This substance is prepared in large quantities, principally for the use of the perfumer, by distilling with water the paste of bitter almonds, from which the fixed oil has been expressed. It certainly does not pre-exist in the almonds; the fat oil obtained from them by pressure is absolutely free from every trace of this principle; it is formed by the action of water upon a peculiar crystallizable substance, hereafter to be described, called *amygdalin*, aided in a very extraordinary manner by the presence of the pulpy albuminous matter of the seed. The crude oil has a yellow colour, and contains a very considerable quantity of hydrocyanic acid, the origin of which is contemporaneous with that of the oil itself: it is agitated with dilute solution of protochloride of iron mixed with hydrate of lime in excess, and the whole subjected to distillation; water passes over, accompanied by the purified essential oil, which is to be left for a short time in contact with a few fragments of fused chloride of calcium to free it from water.

Pure hydride of benzoyl is a thin, colourless liquid, of great refractive power, and peculiar and very agreeable odour; its density is 1·043, and its boiling-point 356° (180°C): it is soluble in about 30 parts of water, and is miscible in all proportions with alcohol and ether. Exposed to the air, it greedily absorbs oxygen, and becomes converted into a mass of crystallized benzoic acid. Heated with hydrate of potassa, it disengages hydrogen, and yields benzoate of the base. The vapour of the oil is inflammable, and burns with a bright flame and much smoke. It is very doubtful whether pure bitter-almond oil is poisonous; the crude product, sometimes used for imparting an agreeable flavour to puddings, custards, &c., and even publicly sold for that purpose, is in the highest degree dangerous.

OXIDE OF BENZOYL; BENZOIC ACID; BzO.—This is the sole product of the oxidation at a moderate temperature of bitter-almond oil; it is not, however, thus obtained for the purposes of experiment and of pharmacy. Several of the balsams yield benzoic acid in great abundance, more especially the concrete resinous variety known under the name of gum-benzoin. When

tance is exposed to a gentle heat in a subliming vessel, the benzoic)latilized, and may be condensed by a suitable arrangement. The and most efficient apparatus for this and all)perations is the contrivance of Dr. Mohr: ts of a shallow iron pan, (fig. 171,) over the f which the substance to be sublimed is thinly a sheet of bibulous-paper, pierced with a of pin-holes, is then stretched over the vessel, p made of thick, strong drawing or cartridge- ecured by a string or hoop over the whole. is placed upon a sand-bath and slowly heated equisite temperature; the vapour of the acid s in the cap, and the crystals are kept by the er diaphragm from falling back again into the enzoic acid thus obtained assumes the form of athery, colourless crystals, which exhale a fragrant odour, not g to the acid itself, but due to the small quantity of a volatile oil.

Fig. 171.



productive method of preparing the acid is to mix the powdered gum- very intimately with an equal weight of hydrate of lime, to boil ture with water, and to decompose the filtered solution, concentrated)ration to a small bulk, with excess of hydrochloric acid; the benzoic stallizes out on cooling in thin plates, which may be drained upon a ter, pressed, and dried in the air. By sublimation, which is then with trifling loss, the acid is obtained perfectly white.

ic acid is inodorous when cold, but acquires a faint smell when gently ; it melts just below 212° (100°C), and sublimes at a temperature a ove; it boils at 462° (238°·8C), and emits a vapour of the density It dissolves in about 200 parts of cold, and 25 parts of boiling nd with great facility in alcohol. Benzoic acid is not affected by nitric acid, even at a boiling heat. The crystals obtained by sub- , or by the cooling of a hot aqueous solution, contain an equivalent r, which is basic, or $C_{14}H_5O_3,HO$.

ie benzoates have a greater or less degree of solubility; they are rmed, either directly or by double decomposition. *Benzoates of the* nd of *ammonia* are very soluble, and somewhat difficult to crystallize. *of lime* forms groups of small colourless needles, which require 20 cold water for solution. The salts of *baryta* and *strontia* are soluble ficulty in the cold. Neutral *benzoate of the sesquioxide of iron* is a compound; but the basic salt obtained by neutralizing as nearly as by ammonia a solution of sesquioxide of iron, and then adding ben- ammonia, is quite insoluble. Sesquioxide of iron is sometimes thus ed from other metals in practical analysis. Neutral and basic *of lead* are freely soluble in the cold. *Benzoate of silver* crystallizes transparent plates, which blacken on exposure to light. Some re- le products, obtained by the action of chlorine upon a solution of e of potassa, will be mentioned in the section on the Organic Bases.

)BENZOIC ACID. — When benzoic acid is boiled for several hours with nitric acid, until red fumes cease to appear, it yields a new acid body, h the elements of hyponitric acid are substituted for an equivalent of m of the original benzoic acid. Nitro-benzoic acid greatly resembles acid in character, and contains $C_{14}H_4NO_7,HO=C_{14}(H_4NO_4)O_3,HO$. arkable transformation of the amide of this acid, of *nitro-benzamide,* noticed under the head of aniline.

HOBENZOIC ACID. — Benzoic acid is soluble without change in concen il of vitriol, and is precipitated by the addition of water; it combines, ; with anhydrous sulphuric acid, generating a compound acid analo-

gous to the sulphovinic, but bibasic, forming a neutral and an acid series of salts. The baryta-compound is easily prepared by dissolving in water the viscid mass produced by the union of the two bodies, and saturating the solution with carbonate of baryta. On adding hydrochloric acid to the filtered liquid, and allowing the whole to cool, acid sulphobenzoate of baryta crystallizes out. This salt has an acid reaction, and requires 20 parts of cold water for solution; the neutral salt is much more soluble. The hydrated acid is easily obtained by decomposing the sulphobenzoate of baryta by dilute sulphuric acid; it forms a white, crystalline, deliquescent mass, very stable and permanent, which contains $C_{14}H_5O_3,2SO_3,2HO$.

Benzone, benzophenone.—When dry benzoate of lime is distilled at a high temperature, it yields a thick, oily, colourless liquid, of peculiar odour. This is a mixture of several compounds, from which, however, a crystalline substance $C_{13}H_5O$, or $C_{26}H_{10}O_2$, may be isolated, to which the name *benzone* or *benzophenone* has been given. Carbonate of lime remains in the retort; the reaction is thus perfectly analogous to that by which acetone is produced by the distillation of a dry acetate.

$$CaO,C_{14}H_5O_3=C_{13}H_5O+CaO,CO_2.$$

The benzophenone is, however, always accompanied by secondary products, due to the irregular and excessive temperature, solid hydrocarbons, carbonic oxide, and *benzol*, a body next to be described.

Benzol, or Benzine. — If crystallized benzoic acid be mixed with three times its weight of hydrate of lime, and the whole distilled at a temperature slowly raised to redness in a coated glass or earthen retort, water, and a volatile oily liquid termed *benzol*, pass over, while carbonate of lime, mixed with excess of hydrate of lime, remains in the retort. The benzol separated from the water, and rectified, forms a thin, limpid, colourless liquid, of strong agreeable odour, insoluble in water, but miscible with alcohol, having a density of 0·885, and boiling at 176° (80°C); the sp. gr. of its vapour is 2·738. Cooled to 32° (0°C), it solidifies to a white, crystalline mass. Benzol contains carbon and hydrogen only, in the proportion of 2 eq. of the former to 1 of the latter, or probably $C_{12}H_6$. It is produced by the resolution of the benzoic acid into benzol and carbonic acid, the water taking part in the reaction.

$$C_{14}H_6O_4=C_{12}H_6+2CO_2.$$

Benzol is identical with the bicarbide of hydrogen, many years ago discovered by Mr. Faraday in the curious liquid condensed during the compression of oil-gas, of which it forms the great bulk, being associated with an excessively volatile hydrocarbon, containing carbon and hydrogen in the ratio of the equivalents, the vapour of which required for condensation a temperature of 0° (—17°·7C). This is the substance which has been described under the name of *butylene*, when treating of valeric acid (see page 392).

A copious source of benzol has been lately shown by Mr. Mansfield to exist in the lightest and most volatile portions of coal-tar oil, which will be noticed in its place under the head of that substance.

Sulphobenzide and hyposulphobenzic acid. — Benzol combines directly with anhydrous sulphuric acid, to a thick viscid liquid, soluble in a small quantity of water, but decomposed by a larger portion, with separation of a crystalline matter, the *sulphobenzide*, which may be washed with water, in which it is nearly insoluble, dissolved in ether, and left to crystallize by spontaneous evaporation. It is a colourless, transparent substance, of great importance, fusible at 212° (100°C), bearing distillation without change, and resisting the action of acids and other energetic chemical agents. Sulphobenzide contains $C_{12}H_5SO_2$. It may be viewed as benzol in which 1 eq. of

;en has been replaced by 1 eq. of sulphurous acid. The acid liquid which the preceding substance has been separated, neutralized by ate of baryta and filtered, yields *hyposulphobenzate of baryta*, which is le salt, but crystallizes in an imperfect manner. By double decompo- with sulphate of copper, a compound of the oxide of that metal is d, which forms fine, large, regular crystals. The hydrate of hyposul- zic acid is prepared by decomposing the copper-salt with sulphuretted en; a sour liquid is obtained, which furnishes, by evaporation, a line residue, containing $C_{12}H_5SO_2+HO,SO_3$. The salts of *potassa*, *nmonia*, and of the oxides of *zinc*, *iron*, and *silver*, crystallize freely. mpound acid can be prepared by dissolving benzol in Nordhausen ric acid.

OBENZOL.—Ordinary nitric acid, even at a boiling temperature, has no on benzol; the red fuming acid attacks it, with the aid of heat, with iolence. The product, on dilution, throws down a heavy, oily, yel- and intensely sweet liquid, which has an odour resembling that of lmond oil. Its density is 1·209; it boils at 415° (212°·8C), and dis- not without being slightly changed. It is but little affected by acids, or chlorine, and is quite insoluble in water. Nitrobenzol contains O_4, and may be viewed as benzol, in which 1 eq. of hydrogen is re- by 1 eq. of hyponitric acid. When nitrobenzol is heated with an al- solution of caustic potassa, and the product subjected to distillation, ily liquid passes over: this is a mixture of several substances from on cooling, large red crystals separate, which are nearly insoluble in but dissolve with facility in ether and alcohol. This compound, is called *azobenzol*, melts at 149° (65°), and boils at 379° (192°·2C); ains $C_{12}H_5N$. Together with the azobenzol an oil is produced, which s $C_{12}H_7N$, and has, like ammonia, the power of combining with acids. received the name of *aniline*, and will be described in the section on bases. The reaction which gives rise to azobenzol and aniline in se, is not yet perfectly understood, several other substances being si- eously produced, and a large quantity of nitrobenzol being charred. enzol may, however, be entirely converted into aniline, by a most ele- ocess, discovered by Zinin, namely, by the action of sulphide of am- a, which will be noticed when treating of aniline.

TROBENZOL.—If benzol is dissolved in a mixture of equal volumes of trated nitric and sulphuric acids, and the liquid be boiled for some a, it solidifies on cooling to a mass of crystals, which are easily fu- nsoluble in water, and readily soluble in alcohol. They contain $C_{12}H_4$ $C_{12}(H_42NO_4)$, and may be viewed as benzol in which 2 eq. of hydrogen laced by 2 eq. of hyponitric acid.

ol and chlorine combine when exposed to the rays of the sun; the t is a solid, crystalline, fusible substance, insoluble in water, contain- H_6Cl_6, called *chlorobenzol* When this substance is distilled, it is de- sed into hydrochloric acid, and a volatile liquid, *chlorobenzide*, composed I_3Cl_3.

s chemical relations, benzol exhibits the character of a substance anal- to hydride of methyl (marsh-gas), hydride of ethyl, and hydride of

nzol	$C_{12}H_5H.$=Hydride of Phenyl.
lphobenzol	$C_{12}H_5SO_2$.
itrobenzol	$C_{12}H_5NO_4$.

alcohol belonging to this hydride is known; it contains $C_{12}H_6O_2$=),HO, and will be described among the volatile principles of coal-tar

RIDE OF BENZOYL, *BzCl*.—This compound is prepared by passing dry

chlorine gas through pure bitter-almond oil, as long as hydrochloric acid continues to be formed: the excess of chlorine is then expelled by heat. Chloride of benzoyl is a colourless liquid of peculiar, disagreeable, and pungent odour. Its density is 1·106. The vapour is inflammable, and burns with a tint of green. It is decomposed slowly by cold, and quickly by boiling water, into benzoic and hydrochloric acids; with an alkaline hydrate, benzoate of the base, and chloride of the metal, are generated.

Benzamide.—When pure chloride of benzoyl and dry ammoniacal gas are presented to each other, the ammonia is energetically absorbed, and a white, solid substance produced, which is a mixture of sal-ammoniac and a highly interesting body, *benzamide*. The sal-ammoniac is removed by washing with cold water, and the benzamide dissolved in boiling water, and left to crystallize. It forms colourless, transparent, prismatic, or platy crystals, fusible at 239° (115°C), and volatile at a higher temperature. It is but slightly soluble in cold, freely in boiling water, also in alcohol and ether. Benzamide corresponds to oxamide, both in composition and properties; it contains $C_{14}H_7NO_2 = C_{14}H_5O_3.NH_2$, or benzoate of oxide of ammonium, *minus* 2 eq. of water, and it suffers decomposition by both acids and alkaline solutions, yielding, in the first case, a salt of ammonia and benzoic acid, and, in the second, free ammonia and a benzoate. When distilled it loses again 2 eq. of water, and becomes benzonitrile. (See farther on.)

Iodide of Benzoyl, BzI.—This is prepared by distilling the chloride of benzoyl with iodide of potassium; it forms a colourless, crystalline, fusible mass, decomposed by water and alkalis, in the same manner as the chloride. The *bromide* of benzoyl, BzBr, has very similar properties. The *sulphide*, BzS, is a yellow oil, of offensive smell, which solidifies, at a low temperature, to a soft, crystalline mass. *Cyanide* of benzoyl, BzCy, obtained by heating the chloride with cyanide of mercury, forms a colourless, oily, inflammable liquid, of pungent odour, somewhat resembling that of cinnamon. All these compounds yield benzamide with dry ammonia.

Formobenzoic Acid.—Crude bitter-almond oil is dissolved in water, mixed with hydrochloric acid, and evaporated to dryness: the residue is boiled with ether, which dissolves out the new substance, and leaves sal-ammoniac. Formobenzoic acid forms small, indistinct, white crystals, which fuse, and afterwards suffer decomposition by heat, evolving an odour resembling that of the flowers of the hawthorn, and leaving a bulky residue of charcoal. It is freely soluble in water, alcohol, and ether, has a strong acid taste and reaction, and forms a series of crystallizable salts with metallic oxides. This substance contains $C_{16}H_7O_5.HO = C_{14}H_6O_2 + C_2HO_3.HO$, or the elements of bitter-almond oil, and formic acid: it owes its origin to the peculiar action of strong mineral acids on the hydrocyanic acid of the crude oil, by which that body suffers resolution into formic acid and ammonia. It is decomposed by oxidizing bodies, as binoxide of manganese, nitric acid, and chlorine, into bitter-almond oil and carbonic acid.

Hydrobenzamide.—Pure bitter-almond oil is digested for some hours at about 120° (49°C) with a large quantity of strong solution of ammonia; the resulting white crystalline product is washed with cold ether, and dissolved in alcohol; the solution, left to evaporate spontaneously, deposits the *hydrobenzamide* in regular, colourless crystals, which have neither taste nor smell. This substance melts at a little above 212° (100°C), is readily decomposed by heat, dissolves with ease in alcohol, but is insoluble in water; the alcoholic solution is resolved by boiling into ammonia and bitter-almond oil; a similar change happens with hydrochloric acid. Hydrobenzamide contains $C_{42}H_{18}N_2$, or the elements of 3 equivalents of bitter-almond oil, and 2 of ammonia, *minus* 6 equivalents of water. When impure bitter-almond oil is employed in this experiment, the products are different, several other com-

ıds being obtained. But even with the pure oil frequently a great variety ıbstances are formed. The hydrobenzamide when submitted to the action ıemical processes furnishes a great number of derivatives, of which, how-, only one substance, namely, *amarine*, will be described in the section he organic bases.

ENZOIN. — This substance is found in the residue contained in the retort ı which bitter-almond oil has been distilled with lime and oxide of iron, ee it from hydrocyanic acid; it is a product of the action of alkalis and line earths on the crude oil, and is said to be only generated in the ence of hydrocyanic acid. It is easily extracted from the pasty mass, by lving out the lime and oxide of iron by hydrochloric acid, and boiling residue in alcohol. Benzoin forms colourless, transparent, brilliant, natic crystals, tasteless and inodorous; it melts at 248° (120°C), and ls without decomposition. Water, even at a boiling heat, dissolves but all quantity of this body; boiling alcohol takes it up in a larger propor-; it dissolves in cold oil of vitriol, with violet colour. Benzoin contains $_6O_2$, or $C_{28}H_{12}O_4$, and is, consequently, an isomeric modification of bitter-nd oil.

NZILE.—This curious compound is a product of the action of chlorine on oin; the gas is conducted into the fused benzoin as long as hydrochloric continues to be evolved. It is likewise formed by treating benzoin with ng nitric acid. The crude product is purified by solution in alcohol. It s large, transparent, sulphur-yellow crystals, fusible at 200° (93°·3C), ered by distillation, and quite insoluble in water. It dissolves freely in ıol, ether, and concentrated sulphuric acid, from which it is precipitated ater. Benzile is composed of $C_{14}H_5O_2$, or $C_{28}H_{10}O_4$, and is therefore *iso- with the radical of the benzoyl-series.*

NZOLIC ACID. — Benzoin and benzile dissolve with the violet tint in an ıolic solution of caustic potassa; by long boiling the liquid becomes ırless, and is then found to contain a salt of a peculiar acid, called the *'ic*, which is easily obtained by adding hydrochloric acid to the filtered 1, and leaving the whole to cool. Benzilic acid forms small, colourless, parent crystals, slightly soluble in cold, more readily in boiling water; lts at 248° (120°C), and cannot be distilled without decomposition. It lves in cold concentrated sulphuric acid with a fine carmine-red colour. ilic acid contains $C_{28}H_{11}O_5$,HO, or 2 eq. benzile and 1 eq. water.

NZONITRILE.—When benzoate of ammonia is exposed to destructive dision, among other products a yellowish volatile oil makes its appearance, ıg exactly the odour of bitter-almond oil. It is heavier than water, tly soluble in that liquid, boils at 376° (191°·1C), and contains $C_{14}H_5N$. benzoate of ammonia,—4 eq. of water, ($NH_4O,C_{14}H_5O_3—4HO=C_{14}H_5N$,) stands to this salt in the same relation as cyanogen to oxalate, hydroic acid to formate, and cyanide of methyl to acetate of ammonia. Benrile likewise may be viewed as a cyanide, when it becomes a member of henyl-series, $C_{14}H_5N=C_{12}H_5C_2N$.

NZOYL. — Benzoate of copper by dry distillation cautiously conducted a residue containing salicylic and benzoic acids, and an oily distilled uct which crystallizes on cooling. This substance possesses the odour e geranium, melts at 158° (70°C), and contains $C_{14}H_5O_2$. It was dised by Ettling, and subsequently studied by Stenhouse, and is evidently adical of the benzoyl-series. By heating with hydrate of potassa it is ntly converted into benzoic acid with disengagement of hydrogen.

NZIMIDE. — This is a white, inodorous, shining, crystalline substance ionally found in crude bitter-almond oil. It is insoluble in water, and lightly dissolved by boiling alcohol and ether. Oil of vitriol dissolves it lark indigo-blue colour, becoming green by the addition of a little water.

This reaction is characteristic. Benzimide contains $C_{28}H_{11}NO_4$. It may be viewed as derived from an acid benzoate of ammonia by the separation of 4 eq. of water.

A great number of other compounds derived from bitter-almond oil, directly or indirectly, have been described by M. Laurent and others. Many of these contain sulphur, sulphuretted hydrogen and sulphide of ammonium being employed in their preparation.

Hippuric acid.—This interesting substance is in some measure related to the benzoyl-compounds. It occurs, often in large quantity, in combination with potassa or soda, in the urine of horses, cows, and other graminivorous animals. It is prepared by evaporating in a water-bath perfectly fresh cow-urine to about a tenth of its volume, filtering from the deposit, and then mixing the liquid with excess of hydrochloric acid. Cow-urine frequently deposits hippuric acid without concentration, when mixed with a considerable quantity of hydrochloric acid, in which the acid is less soluble than in water. The brown crystalline mass which separates on cooling is dissolved in boiling water, and treated with a stream of chlorine gas until the liquid assumes a light amber colour, and begins to exhale the odour of that substance: it is then filtered, and left to cool. The still impure acid is re-dissolved in water, neutralized with carbonate of soda, and boiled for a short time with animal charcoal; the hot filtered solution is, lastly, decomposed by hydrochloric acid.

Hippuric acid in a pure state crystallizes in long, slender, milk-white, and exceedingly frangible square prisms, which have a slight bitter taste, fuse on the application of heat, and require for solution about 400 parts of cold water; it also dissolves in hot alcohol. It has an acid reaction, and forms salts with bases, many of which are crystallizable. Exposed to a high temperature, hippuric acid undergoes decomposition, yielding benzoic acid, benzoate of ammonia, and a fragrant oily matter, with a coaly residue. With hot oil of vitriol, it gives off benzoic acid: boiling hydrochloric acid converts it into benzoic acid and glycocine (gelatin-sugar) which is described in the Section on Animal Chemistry. Hippuric acid contains $C_{18}H_8NO_5,HO$.

The constitution of hippuric acid has been frequently discussed by chemists. Very different views have been proposed. The most probable one is, that it is the amidogen compound of a peculiar acid—glycobenzoic acid. If hippuric acid be treated with nitrous acid, it undergoes the decomposition peculiar to amidogen-compounds, which has been explained when treating of oxamide (page 343). A new non-nitrogenous acid is formed together with water and pure nitrogen $C_{18}H_8NO_5,HO+NO_3=C_{18}H_7O_7,HO+HO+2N$. Glycobenzoic acid is a crystalline substance, slightly soluble in water, but readily dissolved by alcohol and ether. It may be viewed as a conjugate acid, containing benzoic and glycolic acids — 2 eq. of water $C_{18}H_7O_7,HO=C_{14}H_6O_4,C_4H_4O_6-2HO$. Under the influence of boiling water it splits indeed into benzoic and glycolic acids. Glycocine must be considered as glycolamide $NH_4O,C_4H_3O_5-2HO=C_4H_5NO_4$, and this explains the conversion of hippuric acid into benzoic acid and glycocine.

If, in the preparation of hippuric acid, the urine be in the slightest degree putrid, the hippuric acid is all destroyed during the evaporation, ammonia is disengaged in large quantity, and the liquid is then found to yield nothing but benzoic acid, not a trace of which can be discovered in the unaltered secretion. Complete putrefaction effects the same change; benzoic acid might thus be procured to almost any extent.

When benzoic acid is taken internally, it is rejected from the system in the state of hippuric acid, which is then found in the urine.

HOMOLOGUES OF THE BENZOYL-SERIES.

Toluylic Acid, $C_{16}H_7O_3,HO$. — This substance, which differs from benzoic acid by C_2H_2, has been lately discovered by Mr. Noad, who obtained it by the action of very dilute nitric acid upon cymol, a carbo-hydrogen occurring in cumin-oil. It is a substance exhibiting the closest analogy with benzoic acid both in its physical characters and in its chemical relations. Like benzoic acid, when treated with fuming nitric acid, it yields a nitro-acid, nitrotoluylic acid, $C_{16}H_6NO_7,HO = C_{16}(H_6NO_4)O_3,HO$; distilled with lime or baryta, it furnishes a hydro-carbon $C_{14}H_8$, homologous to benzol. The latter substance, which has received the name of *toluol*, is also obtained from other sources, especially from coal-tar and Tolu balsam.

An acid of the formula $C_{18}H_9O_3,HO$, is not yet known, but we may confidently expect that the progress of science will not fail to elicit this substance; even now we are acquainted with a hydrocarbon $C_{16}H_{10}$, homologous to benzol and toluol. This substance, which is called *xylol*, is found in wood-tar and coal-gas-naptha, and stands to the unknown acid $C_{18}H_9O_3HO$ in the same relation as benzol to benzoic acid. Should the above acid be discovered, we may with certainty predict that, when distilled with excess of lime, it will yield xylol.

Cumic acid, $C_{20}H_{11}O_3,HO$. — Another acid, homologous to benzoic acid, was discovered some time ago, by MM. Cahours and Gerhardt. It is formed by the oxydation of one of the constituents of cumin-oil, cuminol $C_{20}H_{12}O_2$, which corresponds to oil of bitter almonds. It likewise yields a nitro-acid, nitro-cumic acid $C_{20}H_{10}NO_7,HO = C_{20}(H_{10}NO_4)O_3,HO$, and when distilled is converted into cumol $C_{18}H_{12}$, a hydrocarbon, homologous to benzol, toluol, and xylol.

Of the next series only the hydrocarbon is known. This is cymol $C_{20}H_{14}$, the substance which, as has been mentioned above, is the source of toluylic acid.

The homology of these substances is clearly exhibited by the following table:—

	Hydrides.	Acids.	Hydrocarbons derived from the acid.
Benzoyl-series.........	$C_{14}H_5O_2H$	$C_{14}H_5O_3,HO$	$C_{12}H_6$
Toluyl-series...........		$C_{16}H_7O_3,HO$	$C_{14}H_8$
Xylyl-series............			$C_{16}H_{10}$
Cumyl-series............	$C_{20}H_{11}O_2H$	$C_{20}H_{11}O_3,HO$	$C_{18}H_{12}$
Cymyl-series...........			$C_{20}H_{14}$

This table shows that up to the present moment only the series of hydrocarbons is without a gap, while two acids and three hydrides remain to be discovered.

SALICYL AND ITS COMPOUNDS.

SALICIN. — The leaves and young bark of the poplar, willow, and several other trees contain a peculiar crystallizable, bitter principle, called *salicin*, which in some respects resembles the vegeto-alkalis cinchonine and quinine, being said to have febrifuge properties. It differs essentially, however, from these bodies in being destitute of nitrogen, and in not forming salts with acids. Salicin may be prepared by exhausting the bark with boiling water, concentrating the solution to a small bulk, digesting the liquid with powdered protoxide of lead, and then, after freeing the solution from lead by a stream of sulphuretted-hydrogen gas, evaporating until the salicin crys-

tallizes out on cooling. It is purified by treatment with animal charcoal and re-crystallization.

Salicin forms small, white, silky needles, of intensely bitter taste, which have no alkaline reaction. It melts and decomposes by heat, burning with a bright flame, and leaving a residue of charcoal. It is soluble in 5·6 parts of cold water, and in a much smaller quantity when boiling hot. Oil of vitriol colours it deep red. The last experiments of M. Piria give for salicin the formula $C_{26}H_{18}O_{14}$.

When salicin is distilled with a mixture of bichromate of potassa and sulphuric acid, it yields, among other products, a yellow, sweet-scented oil, *which is found to be identical with the volatile oil distilled from the flowers of the Spiræa ulmaria, or common meadow-sweet.* This substance appears to be the hydride of a compound salt-radical, *salicyl*, containing $C_{14}H_5O_4$; it has the properties of a hydrogen-acid.

Table of Salicyl-Compounds.

Salicyl (symb. Sl)	$C_{14}H_5\ O_4$
Hydrosalicylic acid	$C_{14}H_5\ O_4H$
Salicylide of potassium	$C_{14}H_5\ O_4K$
Hydrochlorosalicylic acid	$C_{14}(H_4Cl)\ O_4H$
Hydriodosalicylic acid	$C_{14}(H_4I)\ O_4H$
Hydrobromosalicylic acid	$C_{14}(H_4Br)O_4H$
Salicylic acid	$C_{14}H_5\ O_5,HO$

HYDROSALICYLIC ACID; SALICYLOUS ACID; ARTIFICIAL OIL OF MEADOW-SWEET, SlH.—One part of salicin is dissolved in 10 of water, and mixed in a retort with 1 part of powdered bichromate of potassa and $2\frac{1}{2}$ parts of oil of vitriol diluted with 10 parts of water; gentle heat is applied, and after the cessation of the effervescence first produced, the mixture is distilled. The yellow oily product is separated from the water, and purified by rectification from chloride of calcium. It is thin, colourless, and transparent, but acquires a red tint by exposure to the air. Water dissolves a sensible quantity of this substance, acquiring the fragrant odour of the oil, and the characteristic property of striking a deep violet colour with a salt of sesquioxide of iron, a property however which is also enjoyed by salicylic acid. Alcohol and ether dissolve it in all proportions. It has a density of 1·173, and boils at 385° (166°·1C), when heated alone. Hydrosalicylic acid decomposes the alkaline carbonates even in the cold; it is acted upon with great energy by chlorine and bromine. By analysis it is found to contain $C_{14}H_6O_4$, or the same elements as crystallized benzoic acid; and the density of its vapour is also the same, being 4·276.

SALICYLIDE OF POTASSIUM, KSl.—This compound is easily prepared by mixing the oil with a strong solution of caustic potassa; it separates, on agitation, as a yellow crystalline mass, which may be pressed between folds of blotting-paper, and re-crystallized from alcohol. It forms large, square, golden-yellow tables, which have a greasy feel, and dissolve very easily both in water and alcohol; the solution has an alkaline reaction. When quite dry, the crystals are permanent in the air; but in a humid state they soon become greenish, and eventually change to a black, soot-like substance, insoluble in water, but dissolved by spirit and by solution of alkali, called *melanic acid.* Acetate of potassa is formed at the same time. Melanic acid contains $C_{20}H_8O_{10}$. The crystals of salicylide of potassium contain water which cannot be expelled without partial decomposition of the salt.

SALICYLIDE OF AMMONIUM, NH_4Sl, crystallizes in yellow needles which are quickly destroyed with production of ammonia and the hydride. *Salicylide of barium*, $BaC_{14}H_5O + 2HO$, forms fine yellow acicular crystals, which are

but slightly soluble in the cold. *Salicylide of copper* is a green insoluble powder, containing $CuC_{14}H_5O_4$.

Salicylide of copper by destructive distillation gives, among other products, hydride of salicyl and a solid body forming colourless prismatic crystals, fusible and volatile. It is insoluble in water, dissolved by alcohol and ether, and is unaffected by fusion with hydrate of potassa. Nitric acid converts it into anilic and picric acids. (See indigo). It contains $C_{14}H_5O_3$, and is isomeric with anhydrous benzoic acid.

CHLOROHYDRO-SALICYLIC ACID, $C_{14}(H_4Cl)O_4.H$.—Chlorine acts very strongly upon the hydride of salicyl; the liquid becomes heated, and disengages large quantities of hydrochloric acid. The product is a slightly yellowish crystalline mass, which, when dissolved in hot alcohol, yields colourless tabular crystals of the pure compound, having a pearly lustre. This substance is insoluble in water; it dissolves freely in alcohol, ether, and solutions of the fixed alkalis; from the latter it is precipitated unaltered by the addition of an acid. It is not even decomposed by long ebullition with a concentrated solution of caustic potassa. Heated in a retort, it melts and volatilizes, condensing in the cool part of the vessel in long, snow-white needles. The odour of this substance is peculiar and by no means agreeable, and its taste is hot and pungent.

Chlorohydro-salicylic acid combines with the metallic oxides; with potassa it forms small red crystalline scales, very soluble in water. The corresponding compound of barium, prepared from the foregoing, by double decomposition, is an insoluble crystalline, yellow powder, containing Ba $C_{14}(H_4Cl)O$.

BROMOHYDRO-SALICYLIC ACID, $C_{14}(H_4Br)O_4.H$.—The bromide-compound is prepared by the direct action of bromine on the hydride of salicyl; it crystallizes in small colourless needles, and very closely resembles in properties the chloride. The hydride of salicyl dissolves a large quantity of iodine, acquiring thereby a brown colour, but forming no combination; the iodide may, however, be procured by distilling iodide of potassium with chlorohydro-salicylic acid. It sublimes as a blackish-brown fusible mass.

CHLOROSAMIDE.—The action of dry ammoniacal gas on pure chlorohydro-salicylic acid is very remarkable; the gas is absorbed in large quantity, and a solid yellow, resinous-looking compound produced, which dissolves in boiling ether, and separates as the solution cools in fine yellow iridescent crystals; this and a little water are the only products, not a trace of sal-ammoniac can be detected. Chlorosamide is nearly insoluble in water; it dissolves without change in ether, and in absolute alcohol; with hot rectified spirit it is partially decomposed, with disengagement of ammonia. Boiled with an acid, it yields an ammoniacal salt of the acid and chlorohydro-salicylic acid; with an alkali, on the other hand, it gives free ammonia, while chlorohydro-salicylic acid remains dissolved. Chlorosamide contains C_{24} $H_{15}Cl_3)N_2O_6$; it is formed by the addition of 2 eq. of ammonia to 3 eq. of chlorohydro-salicylic acid, and the subsequent separation of 6 eq. of water. A corresponding and very similar substance, *bromosamide*, is formed by the action of ammonia on bromohydro-salicylic acid.

SALIGENIN.—This curious substance is a product of the decomposition of salicin under the influence of the emulsion or synaptase of sweet almonds; it is also generated by the action of dilute acids. In both cases the salicin is resolved into saligenin and grape sugar. Saligenin forms colourless, nacreous scales, freely soluble in water, alcohol, and ether. It melts at 180° (82°C), and decomposes at a higher temperature. Dilute acids at a boiling heat convert it into a resinous-looking substance, $C_{14}H_6O_2$, called *saliretin*. Many oxidizing agents, as chromic acid and oxide of silver, convert this substance into hydride of salicyl: even platinum-black produces this effect. Its aqueous solution gives a deep indigo-blue colour with salts of sesquioxide of

iron. Saligenin contains $C_{14}H_8O_4$. Hence the transformation of salicin is represented by the equations:—

$$\underbrace{2C_{26}H_{18}O_{14}+8HO}_{\text{Salicin.}} = \underbrace{C_{24}H_{28}O_{28}}_{\text{Grape-sugar.}} = \underbrace{2C_{14}H_8O_4}_{\text{Saligenin.}}$$

Salicin yields with chlorine substitution-compounds containing that element, which are susceptible of decomposition by synaptase, with production of bodies termed *chloro-* and *bichlorosaligenin.* Chlorosaligenin very closely resembles normal saligenin, and contains $C_{14}(H_7Cl)O_4$. Certain products, called by M. Piria *helicin*, *helicoidin*, and *anilotic acid*, are described as resulting from the action of dilute nitric acid upon salicin. With strong acid at a high temperature *nitro-salicylic acid* (anilic acid) $C_{14}(H_4NO_4)O_5,HO$, is produced.

SALICYLIC ACID, SlO,HO.—This compound is obtained by heating hydride of salicyl with excess of solid hydrate of potassa; the mixture is at first brown, but afterwards becomes colourless; hydrogen gas is disengaged during the reaction. On dissolving the melted mass in water, and adding a slight excess of hydrochloric acid, the salicylic acid separates in crystals, which are purified by re-solution in hot water. This substance very much resembles benzoic acid; it is very feebly soluble in cold water, is dissolved in large quantities by alcohol and ether, and may be sublimed with the utmost ease. It is charred and decomposed by hot oil of vitriol, and attacked with great violence by strong, heated nitric acid. Salicylic acid contains $C_{14}H_5O_5,HO$.

Salicylic acid can also be prepared with great ease by fusing salicin with excess of hydrate of potassa, and also by the action of a concentrated and hot solution of potassa upon the volatile oil of *Gaultheria procumbens*, which is the methyl-compound of this acid occurring in nature (see essential oils containing oxygen). When salicylic acid is mixed with powdered glass or sand and exposed to strong and sudden heat in a retort, it is almost entirely converted into carbonic acid and hydrate of phenyl, $C_{12}H_6O_2$, a substance found in considerable proportion in coal-tar-naphta,—and the same change happens to many of its salts with even greater facility.

PHLORIDZIN.—This is a substance bearing a great likeness to salicin, found in the root-rind of the apple and cherry-tree, and extracted by boiling alcohol. It forms fine, colourless, silky needles, soluble in 1000 parts of cold water, but freely dissolved by that liquid when hot: it is also soluble without difficulty in alcohol. It contains $C_{42}H_{24}O_{20}+4HO$. Dilute acids convert phloridzin into grape-sugar and a crystallizable sweet substance called *phloretin*, $C_{20}H_{14}O_{10}$.

$$\underbrace{2(C_{42}H_{24}O_{20}+4HO)}_{\text{Phloridzin.}} = \underbrace{C_{24}H_{28}O_{28}}_{\text{Grape-sugar.}} + \underbrace{2C_{30}H_{14}O_{10}}_{\text{Phloretin.}}$$

CUMARIN.—The odoriferous principle of the *tonka-bean.* It may be often seen forming minute colourless crystals under the skin of the seed, and between the cotyledons. It is best extracted by macerating the sliced beans in hot alcohol, and, after straining through cloth, distilling off the greater part of the spirit. The syrupy residue deposits on standing crystals of cumarin, which must be purified by pressure from a fat oil which abounds in the beans, and then crystallized from the hot water. So obtained, cumarin forms slender, brilliant, colourless needles, fusible at 122° (50°C), and distilling without decomposition at a higher temperature. It has a fragrant odour and burning taste; it is very slightly soluble in cold water, more

eely in hot water, and also in alcohol. It is unaffected by dilute acids and kalis, which merely dissolve it. Boiling nitric acid converts it into picric cid, and a hot concentrated solution of potassa into *cumaric*, and eventually nto salicylic acid. Cumarin exists in several other plants, as the *Melilotus fficinalis*, the *Asperula adorata*, and the *Anthoxanthum odoratum*. According o M. Bleibtreu it contains $C_{18}H_6O_4$. Cumaric acid is $C_{18}H_8O_6$.

CINNAMYL AND ITS COMPOUNDS.

The essential oil of cinnamon seems to possess a constitution analogous to hat of bitter-almond oil; it passes by oxidation into a volatile acid, the innamic, which resembles in the closest manner benzoic acid. The radical ssumed in these substances bears the name of *cinnamyl;* it has not been solated.

Table of Cinnamyl-Compounds.

Cinnamyl (symbol Ci)	$C_{18}H_7O_2$
Chloride of cinnamyl	$C_{18}H_7O_2Cl$
Hydride of cinnamyl; oil of cinnamon	$C_{18}H_7O_2H$
Hydrated oxide of cinnamyl; cinnamic acid	$C_{18}H_7O_2O,HO$
Cinnamylic alcohol	$C_{18}H_9O,HO$
Cinnamate of cinnamylic ether	$C_{18}H_9O,C_{18}H_7O_3$

Hydride of cinnamyl; oil of cinnamon; CiH.—Cinnamon of excellent uality is crushed, infused twelve hours in a saturated solution of common alt, and then the whole subjected to rapid distillation. Water passes over, ilky from essential oil, which after a time separates. It is collected and ft for a short time in contact with chloride of calcium. This fragrant and ostly substance has, like most of the volatile oils, a certain degree of solubility in water; it is heavier than that liquid, and sinks to the bottom of the eceiver in which the distilled products have been collected. It contains, ccording to M. Dumas, $C_{18}H_8O_2$.

Cinnamic acid, CiO,HO.—When pure oil of cinnamon is exposed to the ir, or inclosed in a jar of oxygen, it is quickly converted by absorption of as into a mass of white crystalline matter, which is hydrated cinnamic acid; his is the only product. Cinnamic acid is found in Peruvian and Tolu balams, associated with benzoic acid, and certain oily and resinous substances; t may be procured by the following process in great abundance, and in a tate of perfect purity. Old, hard Tolu balsam is reduced to powder and ntimately mixed with an equal weight of hydrate of lime; this mixture is oiled for some time in a large quantity of water, and filtered hot. On cooling, cinnamate of lime crystallizes out, while benzoate of lime remains in olution. The impure salt is re-dissolved in boiling water, digested with nimal charcoal, and, after filtration, suffered to crystallize. The crystals re drained and pressed, once more dissolved in hot water, and an excess of ydrochloric acid being added, the whole is allowed to cool; the pure cinamic acid separates in small plates or needle-formed crystals of perfect hiteness. From the original mother-liquor much benzoic acid can be proured.

The crystals of cinnamic acid are smaller and less distinct than those of enzoic acid, which in most respects it very closely resembles. It melts at 48° (120°C), and enters into ebullition and distils without change at 560° 298°·3C); the vapour is pungent and irritating. Cinnamic acid is much ss soluble, both in hot and cold water, than benzoic; a hot saturated soluion becomes on cooling a soft-solid mass of small nacreous crystals. It issolves with perfect ease in alcohol. Boiling nitric acid decomposes cin-

namic acid with great energy, and with production of copious red fumes; bitter-almond-oil distils over, and benzoic acid remains in the retort in which the experiment is made. When cinnamic acid is heated in a retort with a mixture of strong solution of bichromate of potassa and oil of vitriol, it is almost instantly converted into benzoic acid, which afterwards distils over with the vapour of water: the odour of bitter-almond-oil is at the same time very perceptible. The action of chlorine is different; no benzoic acid is formed, but other products, which have not been perfectly studied.

Cinnamic acid forms with bases a variety of salts which are very similar to the benzoates. The crystallized acid contains $C_{18}H_7O_3,HO$. When distilled with an excess of lime or baryta, cinnamic acid undergoes a decomposition analogous to that of benzoic acid; an oily liquid *cinnamol* $C_{16}H_8$ distils over, whilst a carbonate of the alkaline earth remains behind, $C_{18}H_8O_4+2BaO=2(BaO,CO_2)+C_{16}H_8$. This oil is also found in liquid storax, and is frequently described by the term *styrol.* (See resins and balsams.)

CHLOROCINNOSE.—This is the ultimate product of the action of chlorine on oil of cinnamon by the aid of heat. When purified by crystallization from alcohol, it forms brilliant, colourless needles, fusible, and susceptible of volatilization without change. It is not affected by boiling oil of vitriol, and may be distilled without decomposition in a current of ammoniacal gas. Chlorocinnose contains $C_{18}H_4Cl_4O_2$; it is formed by the substitution in the oil of cinnamon of 4 eq. of chlorine for 4 eq. of hydrogen. The true *chloride of cinnamyl*, Ci Cl, seems to be first formed in considerable quantity, and subsequently decomposed by the continued action of the chlorine; it has not been separated in a pure state; it appears as a very thin, fluid oil, convertible into a crystalline mass by strong solution of potassa.

When cinnamon-oil is treated with hot nitric acid, it undergoes decomposition, being converted into hydride of benzoyl and benzoic acid. With a boiling solution of chloride of lime the same thing happens, a benzoate of the base being generated. If the oil be heated with solution of caustic potassa it remains unaffected; with the solid hydrate, however, it disengages pure hydrogen, and forms a potassa-salt, which appears to be the cinnamate. When brought into contact with cold concentrated nitric acid, a crystalline, yellowish, scaly compound is obtained, which is decomposed by water with separation of the oil. With ammonia a solid substance is produced, which also appears to be a direct compound of the two bodies.

Two varieties of oil of cinnamon are met with in commerce of very unequal value, viz. that of China, and that of Ceylon; the former being considered the best: both are, however, evidently impure. The pure oil may be extracted from them by an addition of cold, strong nitric acid; the crystalline matter which forms after the lapse of a few hours, separated and decomposed by water, yields ure hydride of cinnamyl.

There can be no doubt that the cinnamic acid in Tolu and Peru balsams is gradually formed by the oxidation of a substance very closely related to the alcohols. When these balsams are first imported they are nearly fluid, but gradually acquire consistence by keeping. By the aid of an alcoholic solution of potassa, a compound, sometimes oily, sometimes solid, may be separated from these balsams, which cannot be distilled without partial decomposition. This compound, described respectively under the name of *cinnamein* (when oily), and *styracin* (when solid), when distilled with hydrate of potassa, is converted into cinnamic acid and a neutral substance, which likewise occurs in an oily and crystalline modification, and has been called, respectively, *peruvin* and *styrone*. These substances are related to each other in a very remarkable manner. Peruvin may be viewed as the alcohol of

nic acid, when cinnamein becomes the compound ether consisting of l and cinnamic acid. This relation will become obvious by the fol- ; formulæ :—

Ethyl-series.		Cinnamyl-series.	
ohol	C_4H_5O,HO	Peruvin	$C_{18}H_9O,HO$
tic acid	$C_4H_3O_3,HO$	Cinnamic acid.....	$C_{18}H_7O_3,HO$
tic ether	$C_4H_5O,C_4H_3O_3$	Cinnamein	$C_{18}H_9O,C_{18}H_7O_3$

n treated with oxidizing agents, peruvin yields cinnamic acid, or its cts of decomposition, oil of bitter-almonds and benzoic acid.

SECTION III.

VEGETABLE ACIDS.

The vegetable acids constitute a very natural and important family or group of compounds, many of which possess the property of acidity, i.e. acid reaction to litmus paper, and power of forming stable, neutral, and often crystallizable compounds with bases, to an extent comparable with that of the mineral acids. Some of these bodies are very widely diffused through the vegetable kingdom; others are of much more limited occurrence, being found in some few particular plants only, and very frequently in combination with organic alkaline bases, in conjunction with which certain of them will be found described. Many of the vegetable acids are polybasic; and it is remarkable that in the new products, or pyro-acids, to which they often give rise under the influence of heat, this character is usually lost.

The particular acids now to be described are for the most part of extensive and general occurrence; mention will be made of some of the rarer ones in connection with their respective sources.

Table of Vegetable Acids.

Tartaric acid	$C_8H_4O_{10},2HO$
Racemic acid	$C_8H_4O_{10},2HO$
Citric acid	$C_{12}H_5O_{11},3HO$
Aconitic, or equisetic acid	$C_4H\ O_3,HO$
Malic acid	$C_8H_4O_8,2HO$
Fumaric acid	$C_4H\ O_3,HO$
Tannic acid	$C_{18}H_5O_9,3HO$
Gallic acid	$C_7H\ O_3,2HO$

Tartaric acid. — This is the acid of grapes, of tamarinds, of the pine-apple, and of several other fruits, in which it occurs in the state of an acid potassa-salt; tartrate of lime is also occasionally met with. The tartaric acid of commerce is wholly prepared from the *tartar* or *argol*, an impure acid tartrate of potassa, deposited from wine, or rather grape-juice, in the act of fermentation. This substance is purified by solution in hot water, the use of a little pipe-clay, and animal charcoal to remove the colouring-matter of the wine, and subsequent crystallization; it then constitutes *cream of tartar*, and serves for the preparation of the acid. The salt is dissolved in boiling water, and powdered chalk added as long as effervescence is excited, or the liquid exhibits an acid reaction; tartrate of lime and neutral tartrate of potassa result; the latter is separated from the former, which is insoluble, by filtration. The solution of tartrate of potassa is then mixed with excess of chloride of calcium, which throws down all the remaining acid in the form of lime-salt; this is washed, added to the former portion, and then the whole digested with a sufficient quantity of dilute sulphuric acid to withdraw the base and liberate the organic acid. The filtered solution is cautiously evaporated to a syrupy consistence and placed to crystallize in a warm situation.

Tartaric acid forms colourless, transparent crystals, often of large size, ich have the figure of an oblique rhombic prism more or less modified; ese are permanent in the air, and inodorous; they dissolve with great ility in water, both hot and cold, and are also soluble in alcohol. The ution reddens litmus strongly, and has a pure acid taste. The aqueous ution, as has been mentioned (page 76), possesses right-handed polariza-n. This solution is gradually spoiled by keeping. Tartaric acid is basic; the crystals contain $C_8H_4O_{10}, 2HO$. This substance is consumed in ge quantities by the calico-printer, being employed to evolve chlorine from ution of bleaching-powder in the production of white or *discharged* pat-ns upon a coloured ground.

TARTRATE OF POTASSA. NEUTRAL TARTRATE; SOLUBLE TARTAR; $2KO, H_4O_{10}$.—The neutral salt may be procured by neutralizing cream of tartar th chalk, as in the preparation of the acid, or by adding carbonate of tassa to cream of tartar to saturation: it is very soluble, and crystallizes th difficulty in right rhombic prisms, which are permanent in the air, and ve a bitter, saline taste.

ACID TARTRATE OF POTASSA; CREAM OF TARTAR; $KO,HO,C_8H_4O_{10}$.—The igin and mode of preparation of this substance have been already de-ribed. It forms small transparent or translucent prismatic crystals, irre-larly grouped together, which grit between the teeth. It dissolves pretty ely in boiling water, but the greater part separates as the solution cools, aving about $\frac{1}{60}$ or less dissolved in the cold liquid. The salt has an acid action, and a sour taste. When exposed to heat in a close vessel, it is de-mposed with evolution of inflammable gas, leaving a mixture of finely-vided charcoal and pure carbonate of potassa, from which the latter may extracted by water. Cream of tartar is almost always produced when rtaric acid in excess is added to a moderately strong solution of a potassa-lt, and the whole agitated.

TARTRATES OF SODA.—Two compounds of tartaric acid with soda are own: a *neutral salt*, $2NaO,C_8H_4O_{10}+4HO$; and an *acid salt*, $NaO,HO, H_4O_{10}+2HO$. Both are easily soluble in water, and crystallize. Tartaric id and bicarbonate of soda form the ordinary *effervescing draughts*.

TARTRATE OF POTASSA AND SODA; ROCHELLE OR SEIGNETTE SALT; $KO, O,C_8H_4O_{10}+10HO$.—This beautiful salt is made by neutralizing with car-nate of soda a hot solution of cream of tartar, and evaporating to the nsistence of thin syrup. It separates in large, transparent, prismatic ystals, the faces of which are unequally developed; these effloresce slightly the air, and dissolve in $1\frac{1}{2}$ parts of cold water. Acids precipitate cream tartar from the solution. Rochelle salt has a mild, saline taste, and is ed as a purgative.

TARTRATES OF AMMONIA.—The *neutral* tartrate is a soluble and efflorescent t, containing $2NH_4O,C_8H_4O_{10}+2HO$. The *acid* tartrate, $NH_4O,HO,C_8H_4O_{10}$, sely resembles ordinary cream of tartar. A salt corresponding to Rochelle t also exists, having oxide of ammonia in place of soda.

The tartrates of *lime*, *baryta*, *strontia*, *magnesia*, and of the oxides of most the metals proper, are insoluble, or nearly so, in water.

TARTRATE OF ANTIMONY AND POTASSA; TARTAR EMETIC.—This salt is easily de by boiling teroxide of antimony in solution of cream of tartar; it is posited from a hot and concentrated solution in crystals derived from an tahedron with rhombic base, which dissolve without decomposition in 15 rts of cold, and 3 of boiling water, and have an acrid and extremely dis-reeable taste. The solution is incompatible with, and decomposed by, both ids and alkalis; the former throw down a mixture of cream of tartar and roxide of antimony, and the latter, the teroxide, which is again dissolved great excess of the reagent. Sulphuretted hydrogen separates all the

[illegible] Heated in a dry state on charcoal [illegible] a globule of metallic antimony. The crystals [illegible]

[illegible] arsenious acid (AsO_3) in place of tar- [illegible] has been described. It has the same crystalline form as [illegible]

[illegible] tartaric acid dissolves hydrated sesquioxide of iron in large [illegible] which has an acid reaction, and dries up by [illegible] transparent glassy substance, destitute of all traces [illegible] in water, and the solution is not pre- [illegible] Indeed, tartaric acid added in sufficient [illegible] of iron or alumina, entirely prevents [illegible] bases by excess of ammonia. Tartrate and ammoni- [illegible] are used in medicine, these compounds having a less [illegible] preparations.

[illegible] tartaric acid gives white precipitates with lime- and baryta- water [illegible] which dissolve in excess of the acid; with [illegible] no change is produced. The effect on solu- [illegible] has been already noticed.

[illegible] —When crystallized tartaric acid is [illegible] or thereabouts, it melts, loses water [illegible] modifications, called in succession [illegible] acid. The two first are soluble in [illegible] completely different from those [illegible] or anhydrous acid, is a white [illegible] with water, slowly pass into common [illegible] thus expressed:—

[illegible]	$C_8H_4O_{10}.2HO$
[illegible]	$2C_8H_4O_{10}.3HO$
[illegible]	$C_8H_4O_{10}.HO$
[illegible]	$C_8H_4O_{10}$

[illegible] the several modifications of phos- [illegible]

[illegible] —When crystallized tartaric acid is subjected to [illegible] containing this substance passes [illegible] of carbonic acid; in the retort is left [illegible] by farther heating, gives combustible gases [illegible] a residue of charcoal. The distilled product [illegible] acid, and is with great difficulty purified. [illegible] a series of salts, and an ether; it is supposed to con- [illegible] A second pyro-acid sometimes separates in crystals from the [illegible] may be obtained in larger quantity by the destruc- tive [illegible] tartaric; it is composed of $C_5H_3O_3.HO$.

When tartaric acid is heated to 400° (204°.5C) with excess of hydrate of potassa, it is resolved without charring or secondary decomposition into ox- [illegible]

---

[1] According to Dumas, [illegible] Dried at 212° (100°C), an equivalent of water [illegible] equivalents, leaving the compound [illegible] which [illegible] ordinary tartaric acid. Nevertheless, when dissolved in water the crystals again take up the elements of water and reproduce the original salt.

s in union with the base, and only undergo
perature.
- The grapes cultivated in certain
Vosges, in France, contain, in
liar acid body, to which the
soluble than tartaric acid, and
tance. Between these two acids,
nce exists; they have exactly the
sed to heat, the same products; the
e closest manner, with the tartrates.
neutral salt of lime, which is not the
of racemic acid does not rotate the plane

y the subject of some exceedingly interesting
hich have thrown much light upon the relation
If racemic acid be saturated with potassa, or
bases, crystals are obtained, which are identical in
perties. By saturating racemic acid, however, with
g, for instance, compounds corresponding to Rochelle-
potassa and soda or ammonia and soda, and allowing the
allise slowly, two varieties of crystals are produced, which
uished by their form, namely, as the image and the reflection
, or as right-handed and left-handed. If the two kinds of
carefully selected and separately crystallized, in each case crys-
e one variety only are deposited. The composition, the specific
, and, in fact, most of the physical properties of these two varieties
emate of potassa and soda, are invariably the same. They differ, how-
, somewhat in their chemical characters, and especially in one point,
y rotate the plane of polarization in opposite directions. (See page 76.)

M. Pasteur assumes in the two varieties of crystals the existence of two modifications of the same acid, which he distinguishes, according as the salts possess right- or left-handed polarization, by the terms *dextroracemic* and *laevoracemic acids*. These acids can be separated by converting the above compounds into lead- or baryta-salts, and decomposing them by means of sulphuric acid. In this manner two crystalline acids are obtained, identical in every respect excepting in their deportment with polarized light, and in their crystals behaving as image and reflection. It is very probable, not to say certain, that dextroracemic acid is nothing but common tartaric acid. A mixture of equal parts of the two acids has no longer the slightest effect on polarized light, and exhibits in every respect the deportment of racemic acid.

Citric acid.—Citric acid is obtained in large quantity from the juice of limes and lemons; it is found in many other fruits, as in gooseberries, currants, &c., in conjunction with another acid, the malic. In the preparation of this acid, the juice is allowed to ferment a short time, in order that mucilage and other impurities may separate and subside; the clear liquor is then carefully saturated with chalk, which forms, with the citric acid, an insoluble compound. This is thoroughly washed, decomposed by the proper quantity of sulphuric acid, diluted with water, and the filtered solution evaporated to a small bulk, and left to crystallise. The product is drained from the mother-liquor, re-dissolved, digested with animal charcoal, and again concentrated to the crystallising-point. Citric acid forms colourless, prismatic crystals, which have a pure and agreeable acid taste; they dissolve, with great ease, in both hot and cold water; the solution strongly reddens litmus, and, when long kept, is subject to spontaneous change.

Citric acid is tribasic; its formula in the gently dried and anhydrous silver

salt is $C_{12}H_5O_{11}$. The hydrated acid crystallizes with two different quantities of water, assuming two different forms. The crystals, which separate by spontaneous evaporation from a cold saturated solution, contain $C_{12}H_5O_{11}$, $3HO+2HO$, the last being water of crystallization: while, on the other hand, those which are deposited from a hot solution contain but 4 equivalents of water altogether, three of which are basic. Citric acid is entirely decomposed when heated with sulphuric and nitric acids; the latter converts it into oxalic acid. Caustic potassa, at a high temperature, resolves it into acetic and oxalic acids.[1] When subjected to the action of chlorine, the alkaline citrates yield among other products chloroform.

The citrates are very numerous, the acid forming, like ordinary phosphoric acid, three classes of salts, which contain respectively 3 eq. of a metallic oxide, 2 eq. of oxide and 1 eq. of basic water, and 1 eq. oxide and 2 eq. basic water, besides true basic salts, in which the water of crystallization is perhaps replaced by a metallic oxide.

The citrates of the *alkalis* are soluble and crystallizable with greater or less facility; those of *baryta*, *strontia*, *lime*, *lead*, and *silver* are insoluble.

Citric acid resembles tartaric acid in its relations to sesquioxide of iron; it prevents the precipitation of that substance by excess of ammonia. The citrate, obtained by dissolving the hydrated sesquioxide in solution of citric acid, dries up to a pale-brown, transparent, amorphous mass, which is not very soluble in water; an addition of ammonia increases the solubility. Citrate and ammonio-citrate of iron are elegant medicinal preparations. Very little is known respecting the composition of these curious compounds; the absence of crystallization is a great bar to inquiry.

Citric acid is sometimes adulterated with tartaric; the fraud is easily detected by dissolving the acid in a little cold water, and adding to the solution a small quantity of acetate of potassa. If tartaric acid be present, a white crystalline precipitate of cream of tartar will be produced on agitation.

Aconitic, or equisetic acid. — When crystallized citric acid is heated in a retort until it begins to become coloured, and to undergo decomposition, and the fused, glassy product, after cooling, dissolved in water, an acid is obtained, differing completely in properties from citric acid, but identical with an acid extracted from the *Aconitum napellus* and the *Equisetum fluviatile*. Aconitic acid forms a white, confusedly-crystalline mass, permanent in the air, and very soluble in water, alcohol, and ether; the solution has an acid and astringent taste. The salts of aconitic acid possess but little interest; that of *baryta* forms an insoluble gelatinous mass; *aconitate of lime*, which has a certain degree of solubility, is found abundantly in the expressed juice of the *monkshood*, and *aconitate of magnesia* in that of the *equisetum*.

Hydrated aconitic acid contains $C_4HO_3.HO$; it is formed in the artificial process above described, by the breaking up of 1 eq. of hydrated citric acid, $C_{12}H_8O_{14}$, into 2 eq. of water and 3 eq. of hydrated aconitic acid. There are, however, invariably many secondary products formed, such as acetone, carbonic oxide, and carbonic acid. The farther action of heat upon aconitic acid gives rise to several new acids, especially *citraconic* and *itaconic acids*, both expressed by the formula $C_5H_2O_3,HO$. The limits of this elementary work will not permit us to enter into a description of these farther products of decomposition.

Malic acid.—This is the acid of apples, pears, and various other fruits; it is often associated, as already observed, with citric acid. An excellent

[1] The easy resolution of tartaric and citric acids into a mixture of oxalic and acetic acids by the action of heat, aided by the presence of a powerful base, has led to the idea of the possible pre-existence of these last-named bodies in the two vegetable acids, which may thus be *compounded* of two acids of simpler constitution, forming *coupled* or *conjugate acids*, of which *several* have been supposed to exist. These views, although sometimes useful, are not at present supported by evidence of great importance.

ocess for preparing the acid in question is that of Mr. Everitt, who has monstrated its existence, in great quantity, in the juice of the common rden rhubarb; it is accompanied by acid oxalate of potassa. The rhubarb lks are peeled, and ground or grated to pulp, which is subjected to presre. The juice is heated to the boiling-point, neutralized with carbonate potassa, and mixed with acetate of lime; insoluble oxalate of lime falls, hich is removed by filtration. To the clear and nearly colourless liquid, lution of acetate of lead is added as long as a precipitate continues to be oduced. The malate of lead is collected on a filter, washed, diffused rough water, and decomposed by sulphuretted hydrogen.[1] The filtered quid is carefully evaporated to the consistence of syrup, and left in a dry mosphere until it becomes converted into a solid and somewhat crystalline ass of malic acid: regular crystals have not been obtained. From the rries of the mountain-ash (*sorbus aucuparia*) in which malic acid is likese present in considerable quantity, especially at the time they commence ripen, the acid may be prepared by the same process.

Malic acid is bibasic, its formula being $C_8H_4O_8,2HO$; it forms a variety salts, some of which are neutral, others acid. In the presence of fernting substances, especially of putrifying casein, it is itself decomposed, elding succinic, acetic, and carbonic acid.

$$\underbrace{3(C_8H_4O_8,2HO)}_{\text{Malic acid.}} = \underbrace{2(C_8H_4O_6,2HO)}_{\text{Succinic acid.}} + \underbrace{C_4H_3O_3,HO}_{\text{Acetic acid.}} + 4CO_2 + 2HO.$$

metimes also butyric acid and hydrogen are observed among the products this decomposition. Malic acid is colourless, slightly deliquescent, and ry soluble in water; alcohol also dissolves it. The aqueous solution has agreeable acid taste; it becomes mouldy, and spoils by keeping. The ost characteristic of the malates are the *acid malate of ammonia*, $NH_4O,HO,$ H_4O_8, which crystallizes remarkably well, and the *malate of lead*, which is soluble in pure water, but dissolves, to a considerable extent, in warm ute acid, and separates, on cooling, in brilliant, silvery crystals which conn water. The acid may, by this feature, be distinguished. The *acid ma- e of lime*, $CaO,HO,C_8H_4O_8+6HO$, is also a very beautiful salt, freely solu- in warm water. It is prepared by dissolving the sparingly soluble *neutral* alate of lime in hot dilute nitric acid, and leaving the solution to cool.

Recent researches of M. Piria have established a most intimate relation tween malic acid and two substances—asparagin and aspartic acid, which l be described in one of the succeeding sections. These compounds may viewed as malamide and malamic acid, analogous to oxamide and oxamic d.

alic acid[2] . .	$C_4O_6,2HO$	Malic acid . .	$C_8H_4O_8,2HO$
utral oxalate of nmonia . .	$C_4O_6,2NH_4O$	Neutral malate of ammonia . .	$C_8H_4O_8,2NH_4O$
amide . . .	$C_4H_4N_2O_4$	Malamide; asparagin . . .	$C_8H_8N_2O_6$
ioxalate of am- .onia . . .	C_4O_6,HO,NH_4O	Bimalate of ammonia . . .	$C_8H_4O_8,HO,NH_4O$
amic acid .	$C_4H_2N\,O_5,HO$	Malamic acid; aspartic acid .	$C_8H_4NO_7,HO$

[1] If the acid be required pure, crystallized malate of lead must be used, the freshly preciated salt invariably carrying down a quantity of lime, which cannot be removed by simple shing.

[2] We have here doubled the formula of oxalic acid, when it becomes bibasic, like malic acid. re are, in fact, many features in the history of oxalic acid, which render it probable that s bibasic. *In the text we have still* retained the generally received formula.

Hitherto neither asparagin nor aspartic acid have been actually obtained from malic acid. On the contrary, these substances are converted with the greatest facility into malic acid. On passing a current of nitrous acid into a solution of asparagin or aspartic acid, gas is evolved, malic acid being formed.

$$\underbrace{[illegible]}_{\text{Asparagin.}} + [illegible] = \underbrace{[illegible]}_{\text{Malic acid.}} + [illegible]$$

FUMARIC AND MALEIC ACIDS.—If malic acid be heated in a small retort, moderately filled, it melts, emits water, and enters into ebullition; a volatile acid passes over, which dissolves in the water of the receiver. After a time small solid, crystalline scales make their appearance in the boiling liquid and increase in quantity, until the whole becomes solid. The process may now be interrupted, and the contents of the retort, after cooling, treated with cold water: unaltered malic acid is dissolved out, and the new substance, having a smaller degree of solubility, is left behind. It is called fumaric acid, from its identity with an acid extracted from the common fumitory.

Fumaric acid forms small, white, crystalline laminæ, which dissolve freely in hot water and alcohol, but require for that purpose about 200 parts of cold water: it is unchanged by hot nitric acid. When heated in a current of air it sublimes, but in a retort undergoes decomposition. This is a phenomenon often observed in organic bodies of small volatility. Fumaric acid forms salts, which have been examined by M. Rieckher, and an ether, which, by the action of ammonia, yields a white, amorphous, insoluble powder, called *fumaramide*, corresponding in properties and constitution with oxamide. Hydrated fumaric acid contains C_4HO_3,HO; hence it is isomeric with aconitic acid.

The volatile acid produced simultaneously with the fumaric acid is called *maleic acid*: it may be obtained in crystals by evaporation in a warm place. It is very soluble in water, alcohol, and ether: it has a strong acid taste and reaction, and is convertible by heat into fumaric acid. Hydrated maleic acid contains $C_8H_2O_6,2HO$. Maleic and fumaric acids are thus seen to have precisely the same composition: they are formed by the separation of 2 eq. of water from hydrated malic acid.

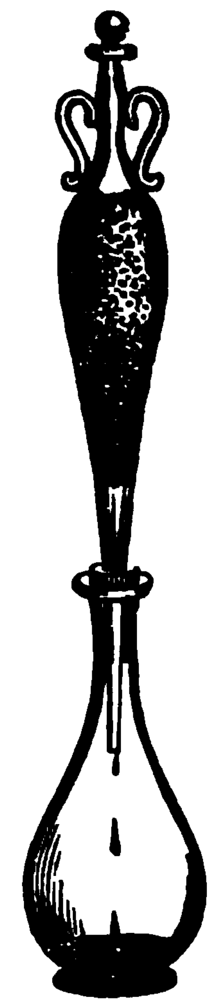
TANNIC AND GALLIC ACIDS.—These are substances in which the acid character is much less strongly marked than in the preceding bodies; they constitute the astringent principles of plants, and are widely diffused, in one form or other, through the vegetable kingdom. It is possible that there may be several distinct modifications of tannic acid, which differ among themselves in some particulars. The astringent principle of oak-bark and nut galls, for example, is found to precipitate salts of sesquioxide of iron bluish black, while that from the leaves of the sumach and tea-plant, as well as infusions of the substances known in commerce under the name of *kino* and *catechu*, are remarkable for giving, under similar circumstances, precipitates which have a tint of green. The colour of a precipitate is, however, too much influenced by external causes to be relied upon as a proof of essential difference. Unfortunately, the tannic acid or acids refuse to crystallize; one most valuable test of individuality is therefore lost.

After the reaction with salts of sesquioxide of iron, the most characteristic feature of tannic acid and the other astringent infusions referred to, is that of forming insoluble compounds with a great variety of organic, and especially animal substances, as solutions of starch and gelatin, solid muscular fibre and skin, &c., which then acquire the property of resisting putre-

tion; it is on this principle that leather is manufactured. Gallic acid, on the contrary, is useless in the operation of tanning.

Tannic Acid of the Oak. — This substance may be prepared by the elegant and happy method of M. Pelouze, from nut-galls, which are excrescences produced on the leaves of a species of oak, the *Quercus infectoria*, by the puncture of an insect. A glass vessel, having somewhat the figure of that represented in the margin, fig. 172, is loosely stopped at its lower extremity by a bit of cotton wool, and half or two-thirds filled with powdered Aleppo-galls. Ether, prepared in the usual manner by rectification, and containing, as it invariably does, a little water, is then poured upon the powder, and the vessel loosely stopped. The liquid, which after some time collects in the receiver below, consists of two distinct strata; the lowest, which is almost colourless, is a very strong solution of nearly pure tannic acid in water; the upper consists of ether holding in solution gallic acid, colouring matter, and other impurities. The carefully-separated heavy liquid is placed to evaporate over a surface of oil of vitriol in the vacuum of the air-pump. Tannic acid, or *tannin*, thus obtained, forms a slightly yellowish, friable, porous mass, without the slightest tendency to crystallization. It is very soluble in water, less so in alcohol, and very slightly soluble in ether. It reddens litmus, and possesses a pure astringent taste without bitterness.

Fig. 172.



A strong solution of this substance mixed with mineral acids gives rise to precipitates, which consist of combinations of the tannic acid with the acids in question; these compounds are freely soluble in pure water, but scarcely so in acid solutions. Tannic acid precipitates albumin, gelatin, salts of the vegeto-alkalis, and several other substances; it forms soluble compounds with the alkalis, which, if excess of base be present, rapidly attract oxygen, and become brown by destruction of the acid; the tannates of *baryta*, *strontia*, and *lime* are sparingly soluble, and those of the oxides of *lead* and *antimony* insoluble. Salts of protoxide of iron are unchanged by solution of tannic acid; salts of the sesquioxide, on the contrary, give with it a deep bluish-black precipitate, which is the basis of writing-ink; hence the value of an infusion of tincture of nut-galls as a test for the presence of that metal. The action of acids upon tannic acid gives rise to the formation of gallic acid, which will be presently described, with simultaneous separation of grape-sugar. Hence tannic acid would appear to be a conjugated sugar-compound.

Tannic acid, carefully dried, contains $C_{18}H_8O_9 + 3HO$.[1]

Tannic acid, closely resembling that obtained from galls, may be extracted by cold water from *catechu;* hot water dissolves out a substance having feeble acid properties, termed *catechin.* This latter compound, when pure, crystallizes in fine colourless needles, which melt when heated, and dissolve very freely in boiling water, but scarcely at all in the cold. Catechin dissolves also in hot alcohol and ether. The aqueous solution acquires a red tint by exposure to air, and precipitates acetate of lead and corrosive sublimate white, reduces nitrate of silver on the addition of ammonia, but fails to form insoluble compounds with gelatin, starch, and the vegeto-alkalis. It

[1] This formula is scarcely established beyond a doubt. M. Strecker, who has observed the formation of sugar from tannic acid, represents this substance by the formula $C_{40}H_{18}O_{26}$, and its change under the influence of acids by the equation

$$\underbrace{2C_{40}H_{18}O_{26} + 8HO}_{\text{Tannic acid.}} = \underbrace{8(C_7HO_3, 2HO)}_{\text{Gallic acid.}} + \underbrace{C_{24}H_{24}O_{24}}_{\text{Grape-sugar.}}$$

strikes a deep green colour with the salts of sesquioxide of iron. This b
is said to be convertible by heat into tannic acid

The formula which has been assigned to catechin is $C_{15}H_6O_6$.

Japonic and *rubic* acids are formed by the action of alkali in excess up
catechin; the first in the caustic condition, and the second when in the st
of carbonate. Japonic acid is a black and nearly insoluble substance, s
luble in alkalis and precipitated by acids, containing $C_{12}H_4O_4.HO$, it a p
haps identical with a black substance of acid properties, formed by
Péligot, by heating grape-sugar with hydrate of baryta. Rubic acid has b
but little studied; it is said to form red insoluble compounds with the e
and certain oxides of the metals.

Several acids closely allied to tannic acid have been found in coffee
Paraguay tea.

Gallic acid.—Gallic acid is not nearly so abundant as tannic acid;
produced by an alteration of the latter. A solution of tannic acid in w
exposed to the air, gradually absorbs oxygen, and deposits crystals of g
acid, formed by the destruction of the tannic acid. The simplest m
of preparing this acid in quantity is to take powdered nut-galls, w
when fresh and of good quality, contain 30 or 40 per cent. of tannic
with scarcely more than a trace of gallic, to mix this powder with wa
a thin paste, and to expose the mixture to the air in a warm situati
the space of two or three months, adding water from time to time to r
that lost by drying up. The mouldy, dark-coloured mass produced
then be strongly pressed in a cloth, and the solid portion boiled in a
siderable quantity of water. The filtered solution deposits on cooling
dance of gallic acid, which may be drained and pressed, and finally p
by re-crystallization. It forms small, feathery, and nearly colourless
tals, which have a beautiful silky lustre; it requires for solution 100
of cold, and only 3 parts of boiling water; the solution has an acid a
tringent taste, and is gradually decomposed by keeping. Gallic acid d
not precipitate gelatin; with salts of protoxide of iron no change is p
duced, but with those of the sesquioxide a deep bluish-black precipit
falls, which disappears when the liquid is heated, from the reduction of
sesquioxide to the protoxide at the expense of the gallic acid.

The salts of gallic acid present but little interest; those of the alkalis
soluble, and readily destroyed by oxidation in presence of excess of b
the solution acquiring after some time a nearly black colour; the salts
of most of the other metallic oxides are insoluble.

Gallic acid, dried at 212° (100°C), contains $C_7HO_3,2HO$; the crystals c
tain an additional equivalent of water.

The insoluble residue of woody fibre and other matters from which
gallic acid has been withdrawn by boiling water, contains a small quan
of another acid substance, which may be extracted by an alkali, and af
wards precipitated by an addition of hydrochloric acid, as a greyish in
luble powder. It contains $C_7H_2O_4$, when dried at 248° (120°C), or ga
acid *minus* 1 eq. of water. The term *ellagic acid* is given to this substa
M. Pelouze once observed its conversion into ordinary gallic acid.

The conversion of tannic into gallic acid by oxidation is accompanied
a disengagement of carbonic acid, the volume of which equals that of
oxygen absorbed: the oxidising action must therefore be confined to the c
bon, and may perhaps be thus represented:—

$$\left.\begin{array}{l}\text{1 eq. tannic acid } C_{18}H_8O_{12}\\ \text{8 eq. oxygen} \ldots\ldots\ldots\ldots O_8\end{array}\right\} = \left\{\begin{array}{ll}\text{2 eq. gallic acid} \ldots\ldots & C_{14}H_6O_{10}\\ \text{2 eq. water} \ldots\ldots\ldots\ldots & H_2O_2\\ \text{4 eq. carbonic acid} & C_4\ \ O_8\end{array}\right.$$

$$C_{18}H_8O_{20} \qquad\qquad C_{18}H_8O_{20}$$

uch of the gallic acid is subsequently destroyed, in all probability only rt of that first produced escaping.

he changes which gallic acid suffers when exposed to heat are very insting. Heated in a retort by means of an oil-bath, the temperature of sh is steadily maintained at 420° (215°C). or thereabouts, it is resolved carbonic acid, and a new acid which sublimes into the neck of the re- in brilliant, crystalline plates, of the most perfect whiteness; an insignant residue of black matter remains behind. The term *pyrogallic acid* iven to the volatile product. It dissolves with facility in water, but the ation cannot be evaporated without blackening and decomposition; it mmunicates a blackish-blue colour to salts of the protoxide of iron, and uces those of the sesquioxide to the state of protoxide. An alkaline solon of this acid absorbs a very considerable quantity of oxygen, and has ely been employed with great advantage by Professor Liebig for the purse of determining the amount of oxygen in atmospheric air. (See page l.) The acid characters of this substance are very indistinct. Pyrogallic l contains $C_6H_3O_3$.

When dry gallic acid is suddenly heated to 480° (249°C), or above, it is omposed into carbonic acid, water, and a second new acid, the *metagallic*, ch remains in the retort as a black, shining mass, resembling charcoal; w crystals of pyrogallic acid are formed at the same time. Metagallic l is insoluble in water, but dissolves in alkalis, and is again precipitated a black powder by the addition of an acid. It combines with the oxides ead and silver, and is composed of $C_6H_2O_2$. Pyrogallic acid, also, exposed he requisite temperature, yields metagallic acid, with separation of water. annic acid, under similar circumstances, furnishes the same products as ic acid. Dr. Stenhouse has shown that pyrogallic acid may be procured onsiderable quantity by carefully heating the dried aqueous extract of -nuts in Dr. Moh's subliming apparatus, already described. All these nges admit of simple explanation.

$$\underbrace{C_7H_3O_5}_{\text{Dry gallic acid.}} = \underbrace{C_6H_3O_3}_{\text{Pyrogallic acid.}} + CO_2$$

$$\underbrace{C_6H_3O_3}_{\text{Pyrogallic acid.}} = \underbrace{C_6H_2O_2}_{\text{Metagallic acid.}} + \underbrace{HO}$$

$$\underbrace{3(C_{18}H_5O_9,3HO)}_{\text{Tannic acid.}} = \underbrace{6(C_7HO_3,2HO)}_{\text{Gallic acid.}} + \underbrace{2C_6H_3O_3}_{\text{Pyrogallic acid.}}$$

These phenomena present admirable illustrations of the production of ogen-acids by the agency of heat.

SECTION IV.

[illegible] SIMPLE CONSTITUTION.

[illegible] AND DERIVATIVES.

[illegible] of a quasi-simple sub-radical that [illegible] class: it is interesting [illegible]

[illegible] with the utmost ease by heating in a small [illegible] mercury, previously reduced to [illegible] undergoes decomposition, like the [illegible] metallic mercury, a small quan- [illegible] again be made, and cyanogen [illegible] which must be collected over mercury. [illegible] resembling that of peach- [illegible] while at the temperature of 45° [illegible] condenses to a thin, colourless, [illegible] with a beautiful pur- [illegible] liberating [illegible] equivalent [illegible] with twice its mea- [illegible] volume of nitrogen [illegible] capacity of [illegible] less than 4 or 5 times its [illegible] the solution [illegible] $N + 4H_2O = NH_4(C_2O_4)$, [illegible]

[illegible]—[illegible] substance above referred [illegible] with cyanogen is prepared by [illegible] by the decomposition of [illegible] It is insoluble in water and [illegible] temperature, and contains, according to [illegible] carbon and nitrogen in the same proportions as in cya- [illegible]

[illegible] PRUSSIC ACID, HCy.—This very [illegible] properties, was [illegible] prepared in a state of purity [illegible] A [illegible] glass tube filled with dry [illegible] the extremity with an arrangement [illegible] tube attached [illegible] necked phial plunged in [illegible] is applied to the tube, the contents of which

[illegible] generate.

ter decomposition in contact with the gas, sulphide of mercury and cyanide of hydrogen being produced: the latter is condensed in the receiver to liquid form. A little of the cyanide of mercury should be left undecomposed, to avoid contamination of the product by sulphuretted hydrogen. The pure acid is a thin, colourless, and exceedingly volatile liquid, which has a density of 0·7058 at 45° (7°·6C), boils at 79° (26°·1C), and solidifies when cooled to 0° (—17°·8C); its odour is very powerful and most characteristic, much resembling that of peach-blossoms or bitter-almond oil; it has a very feeble acid reaction, and mixes with water and alcohol in all proportions. In the anhydrous state this substance constitutes one of the most formidable poisons known, and even when largely diluted with water, its effects upon the animal system are exceedingly energetic: it is employed, however, in medicine in very small doses. The inhalation of the vapour should be carefully avoided in all experiments in which hydrocyanic acid is concerned, as it produces headache, giddiness, and other disagreeable symptoms; ammonia and chlorine are the best antidotes.

The acid in its pure form can seldom be preserved; even when enclosed in a carefully-stopped bottle it is observed after a very short time to darken, and eventually to deposit a black substance containing carbon, nitrogen, and perhaps hydrogen; ammonia is formed at the same time, and many other products. Light favours this decomposition. Even in a dilute condition it is apt to decompose, becoming brown and turbid, but not always with the same facility, some samples resisting change for a great length of time, and then suddenly solidifying to a brown, pasty mass in a few weeks.

When hydrocyanic acid is mixed with concentrated mineral acids, the hydrochloric for example, the whole solidifies to a crystalline paste of sal-ammoniac and hydrated formic acid; a reaction which is explained in a very simple manner, 1 eq. of hydrocyanic acid and 4 eq. water, yielding 1 eq. of ammonia and 1 eq. of formic acid.

$$C_2N,H + 4HO = NH_3 + C_2HO_3.HO$$

On the other hand, when dry formate of ammonia is heated to 392° (200°C), it is almost entirely converted into hydrocyanic acid and water.

$$NH_4O,C_2HO_3 = C_2N,H + 4HO.$$

Aqueous solution of hydrocyanic acid may be made by various means. The most economical, and by far the best, where considerable quantities are wanted, is to decompose at a boiling-heat the yellow ferrocyanide of potassium by diluted sulphuric acid. For example, 500 grains of the powdered ferrocyanide may be dissolved in four or five ounces of warm water, and introduced into a capacious flask or globe capable of being connected by a perforated cork and wide bent tube with a Liebig's condenser well supplied with cold water; 300 grains of oil of vitriol are diluted with three or four times as much water and added to the contents of the flask; distillation is carried on until about one-half of the liquid has distilled over, after which the process may be interrupted. The theory of this process has been carefully studied by Mr. Everitt;[1] it is sufficiently complicated.

eq. ferrocyanide of potassium	6 eq. carbon	Insoluble yellow salt.
	6 eq. carbon	
	3 eq. nitrogen	
	3 eq. nitrogen	
	1 eq. potassium	
	3 eq. potassium	
	2 eq. iron	
eq. water	3 eq. hydrogen	3 eq. hydrocyanic acid.
	3 eq. oxygen	
eq. sulphuric acid		3 eq. bisulphate of potassa.

[1] Phil. Magazine, Feb. 1835.

...am as *insoluble yellow*
...*with* the bisulphate of p...
...*iron*, and 1 eq. cyanide
...*n* exposure to the air, it

...*r* purposes of pharmacy, it is
...*er* above described, and then
...*ute* it with pure water to the
...*cent.* of real acid. This exam...
...*excess* of nitrate of silver a know...
...*the* insoluble cyanide of silver upo...
...*ing*, drying, and lastly re-weighing t...
...*e that* of the hydrocyanic acid can
...*the* one corresponding to an equival...
...*e* cyanide of silver may be divided b...
...*ion* to the truth.
...*ethod* for determining the amount of hy...
...*ately* suggested by Prof. Liebig. It is b...
...*by* cyanide of potassium of dissolving a q...
...*cient* to produce with it a double cyanide ...
...*anide* of silver and of potassium (KCy,AgC...
...*anic* acid, which is super-saturated with po...
...*rops* of solution of common salt, will not yield
...*th* nitrate of silver before the whole of the hy...
...*into* the above double salt. If we know the a...
...*olume* of the nitrate-solution, it is easy to calc...
...*rocyanic* acid, for this quantity will stand to the a...
...*rate* consumed, as 2 eq. of hydrocyanic acid to

$$108 : 54 = \text{silver consumed} : x.$$

...*a* remark, that the hydrocyanic acid made from fer...
...*keeps* better than that made by other means. The
...*to* the presence of a trace of mineral acid. Mr. E...
...*at* a few drops of hydrochloric acid, added to a larg...
...*acid*, preserved it from decomposition, while anothe...
...*i*, became completely spoiled.
...*venient* process for the extemporaneous preparation o...
...*strength*, is to decompose a known quantity of cyanide ...
...*tion* of tartaric acid: 100 grains of crystallized tartar...
...*rains* of cyanide of potassium, and 2 measured ounces of
...*en* up in a phial for a few seconds, and then left at rest,
...*recipitate* may subside, will yield an acid of very nearly the
...*A* little alcohol may be added to complete the separatio...
...*artar*; no filtration or other treatment need be employed.
...*uction* of hydrocyanic acid from bitter-almonds has been
...*in* connection with the history of the volatile oil. Bitter-...
...*of* plums and peaches, the seeds of the apple, the leav...
...*el*, and various other parts of plants belonging to the grea...
...*r*, yield on distillation with water, a sweet-smelling liq...
...*irocyanic* acid. This is probably due in all cases to the d...
...*the amygdalin*, pre-existent in the organic structure. The
...*ion* is brought about, in a very singular manner, by the pre...
...*uble* azotized substance, called *emulsin* or *synaptase*, which ...
...*portion* of the white pulp of both bitter and sweet almonds. T...
...*stance* bears a somewhat similar relation to amygdalin, that diastas...

AZOTIZED ORGAN...

CYA...

CYANOGEN [1] forr...
chemistry presen...
also from being ...
Cyanogen m...
retort of hard ...
powder, and ...
oxide under ...
tity of a brov...
itself, a colo...
It has a pu...
kernels, or ...
(7°·2C) to ...
transpare...
ple, or pe...
nitrogen. ...
and nitr...
of the la...
sure of ...
is form...
equal t...
elemen...
volum...
rapidl...
brow...
Pa...
to, w...
heat...
solu...
alco...
Pro...
nog...
C...
im...
ver...
an...
cy...
fu...
th...
fre...

ıy particulars, does to starch. Hydrocyanic acid ·nsiderable extent in the juice of the bitter cassava. ɹ with facility by the following process:—The paste which the fixed oil has been expressed, is exhausted this coagulates and renders inactive the synaptase, ıe it dissolves out the amygdalin. The alcoholic liquid ·er-bath, by which much of the spirit is recovered, and · diluted with water, mixed with a little yeast, and set in ferment; a portion of sugar, present in the almonds, is thus ·e filtered liquid is then evaporated to a syrupy state in a ıd mixed with a quantity of alcohol, which throws down the ıs a white crystalline powder; the latter is collected on a cloth ɜed, re-dissolved in boiling alcohol, and left to cool. It separates crystalline plates, of pearly whiteness, which are inodorous and ısteless; it is decomposed by heat, leaving a bulky coal, and diffusing ır of the hawthorn. In water, both hot and cold, amygdalin is very ɜ: a hot saturated solution deposits, on cooling, brilliant prismatic which contain water. In cold alcohol it dissolves with great diffi- Heated with dilute nitric acid, or a mixture of dilute sulphuric acid ɔxide of manganese, it is resolved into ammonia, bitter-almond oil, acid, formic acid, and carbonic acid; with permanganate of potassa, a mixture of cyanate and benzoate of that base.

dalin is composed of $C_{40}H_{27}NO_{22}$.

ıtase itself has never been obtained in a state of purity, or fit for ; it is described as a yellowish-white, opaque, brittle mass, very in water, and coagulable, like albumin, by heat, in which case it specific property. In solution it very soon becomes turbid and pu- The decomposition of amygdalin under the influence of this body ɜlegantly studied by dissolving a portion in a large quantity of water, ing a little emulsion of sweet-almond; the odour of the volatile oil ·tely becomes apparent, and the liquor yields, on distillation, hydro- cid. The nature of the decomposition may be thus *approximately* ıted:—

$$
\begin{array}{ll}
\text{1 eq. amygdalin,} & \left\{\begin{array}{lr}
\text{1 eq. hydrocyanic acid} & C_{2}H\,N \\
\text{2 eq. bitter-almond oil} & C_{28}H_{12}\,O_{4} \\
\text{sugar} \ldots\ldots\ldots\ldots & C_{6}H_{7}\,O_{7} \\
\text{2 eq. formic acid} \ldots\ldots & C_{4}H_{2}\,O_{6} \\
\text{5 eq. water} \ldots\ldots\ldots\ldots & H_{5}\,O_{5}
\end{array}\right. \\
C_{40}H_{27}NO_{22} & \\
& \qquad\qquad\qquad\qquad\qquad \overline{C_{40}H_{27}NO_{22}.}
\end{array}
$$

y be observed that in preparing bitter-almond oil the paste should mixed with about 20 parts of warm water, and the whole left to me hours before distillation; the heat must be gently raised to avoid ɜing the synaptase before it has had time to act upon the amygdalin. -paste, thrown into boiling water, yields little or no bitter-almond oil.

DALIC ACID.—When amygdalin is boiled with an alkali or an earth, it is decomposed into ammonia, and a new acid called the *ic*, which remains in union with the base. This is best prepared by f baryta-water, the ebullition being continued as long as ammonia ed. From the solution thus obtained, the baryta may be precipi- y dilute sulphuric acid; the filtered liquid is evaporated in a water- Amygdalic acid forms a colourless, transparent, amorphous mass, uble in water, and deliquescent in moist air; the solution has an *te and reaction. It is* converted by oxidizing agents into bitter-

almond oil, formic, and benzoic acids. The amygdalates are mostly soluble, but have been but little studied; the acid contains $C_{40}H_{26}O_{24}$, HO.

The presence of hydrocyanic acid is detected with the utmost ease; its remarkable odour and high degree of volatility almost sufficiently characterise it. With solution of nitrate of silver it gives a dense curdy white precipitate, much resembling the chloride, but differing from that substance in not blackening so readily by light, in being soluble in boiling nitric acid, and in suffering complete decomposition when heated in a dry state, metallic silver being left; the chloride, under the same circumstances, merely fuses, but undergoes no chemical change. The production of Prussian blue by "Scheele's test" is an excellent and most decisive experiment, which may be made with a very small quantity of acid. The liquid to be examined is mixed with a few drops of solution of sulphate of protoxide of iron and an excess of caustic potassa, and the whole exposed to the air for 10 or 15 minutes, with agitation; hydrochloric acid is then added in excess, which dissolves the oxide of iron, and, if hydrocyanic acid be present, leaves Prussian blue as an insoluble powder. The reaction becomes quite intelligible when the production of a ferrocyanide, described a few pages back, is understood. See page 482.

Another elegant process for detecting hydrocyanic acid is mentioned in the article upon hydrosulphocyanic acid.

The most important of the metallic cyanides are the following; they bear the most perfect analogy to the haloid-salts.

Cyanide of Potassium, KCy.—When potassium is heated in cyanogen gas, it takes fire and burns in a very beautiful manner, yielding cyanide of the metal; the same substance is produced when potassium is heated in the vapour of hydrocyanic acid, hydrogen being liberated. If pure nitrogen gas be transmitted through a white-hot tube, containing a mixture of carbonate of potassa and charcoal, a considerable quantity of cyanide of potassium is formed, which settles in the cooler portions of the tube as a white amorphous powder; carbonic oxide is at the same time extricated. If azotized organic matter of any kind, capable of furnishing ammonia by destructive distillation, as horn-shavings, parings of hides, &c., be heated to redness with carbonate of potassa in a close vessel, a very abundant production of cyanide of potassium results, which cannot however be advantageously extracted by direct means, but in practice is always converted into ferrocyanide, which is a much more stable substance, and crystallizes better.

There are several methods by which cyanide of potassium may be prepared for use. It may be made by passing the vapour of hydrocyanic acid into a cold alcoholic solution of potassa; the salt is deposited in a crystalline form, and may be separated from the liquid, pressed and dried. Ferrocyanide of potassium, heated to whiteness in a nearly close vessel, evolves nitrogen and other gases, and leaves a mixture of charcoal, carbide of iron, and cyanide of potassium, which latter salt is not decomposed unless the temperature be excessively high. Mr. Donovan recommends the use in this process of a wrought-iron mercury-bottle, which is to be half filled with the ferrocyanide, and arranged in a good air-furnace, capable of giving the requisite degree of heat; a bent iron tube is fitted to the mouth of the bottle and made to dip half an inch into a vessel of water; this serves to give exit to the gas. The bottle is gently heated at first, but the temperature ultimately raised to whiteness; when no more gas issues, the tube is stopped with a cork, and, when the whole is completely cold, the bottle is cut asunder in the middle by means of a chisel and sledge-hammer, and the pure white fused salt carefully separated from the black spongy mass below, and preserved in a well-stopped bottle; the black substance contains much

yanide, which may be extracted by a little cold water. It would be better, erhaps, in the foregoing process, to deprive the ferrocyanide of potassium f its water of crystallization before introducing it into the iron vessel.

Professor Liebig has published a very easy and excellent process for aking cyanide of potassium, which does not, however, yield it pure, but iixed with cyanate of potassa. For most of the applications of cyanide f potassium, as, for example, electro-plating and gilding, for which a conidereable quantity is now required, this impurity is of no consequence. 8 arts of ferrocyanide of potassium are rendered anhydrous by gentle heat, nd intimately mixed with 3 parts of dry carbonate of potassa; this mixare is thrown into a red-hot earthen crucible, and kept in fusion, with occaional stirring, until gas ceases to be evolved, and the fluid portion of the iass becomes colourless. The crucible is left at rest for a moment, and hen the clear salt decanted from the heavy black sediment at the bottom, hich is principally metallic iron in a state of minute division. In this xperiment, 2 eq. of ferrocyanide of potassium and 2 eq. carbonate of otassa yield 5 eq. cyanide of potassium, 1 eq. cyanate of potassa, 2 eq. ron, and 2 eq. carbonic acid. The product may be advantageously used, nstead of ferrocyanide of potassium, in the preparation of hydrated hydroyanic acid, by distillation with diluted oil of vitriol.

Cyanide of potassium forms colourless, cubic or octahedral crystals, deliquescent in the air, and exceedingly soluble in water; it dissolves in boiling lcohol, but separates in great measure on cooling. It is readily fusible, and ndergoes no change at a moderate red, or even white-heat, when excluded rom air; otherwise, oxygen is absorbed and the cyanide of potassium ecomes cyanate of potassa. Its solution always has an alkaline reaction, nd exhales when exposed to the air the smell of hydrocyanic acid; it is ecomposed by the feeblest acids, even the carbonic acid of the atmosphere, nd when boiled in a retort is slowly converted into formate of potassa with eparation of ammonia. This salt is anhydrous; it is said to be as poisonous s hydrocyanic acid itself.

Cyanide of potassium has been derived from a curious and unexpected ource. In some of the iron-furnaces in Scotland where raw-coal is used or fuel with the hot blast, a saline-looking substance is occasionally observed o issue in a fused state from the tuyere-holes of the furnace, and concrete n the outside. This proved, on examination by Dr. Clark, to be principally yanide of potassium.

Cyanide of sodium, NaCy, is a very soluble salt, corresponding closely ith the foregoing, and obtained by similar means.

Cyanide of ammonium, NH_4Cy. — This is a colourless, crystallizable, and ery volatile substance, prepared by distilling a mixture of cyanide of potasium and sal-ammoniac, or by mingling the vapour of anhydrous hydrocyanic cid with ammoniacal gas, or, lastly, according to the observation of M. anglois, by passing ammonia over red-hot charcoal. It is very soluble in rater, subject to spontaneous decomposition, and is highly poisonous.

Cyanide of mercury, HgCy. — One of the most remarkable features in he history of cyanogen is its powerful attraction for certain of the less xidable metals, as silver, and more particularly mercury and palladium. Dilute hydrocyanic acid dissolves finely-powdered red oxide of mercury with he utmost ease; the liquid loses all odour, and yields on evaporation crysals of cyanide of mercury. Cyanide of potassium is in like manner decomosed by red oxide of mercury, hydrate of potassa being produced. Cyanide f mercury is generally prepared from common ferrocyanide of potassium; parts of the salt are dissolved in 15 parts of hot water, and 3 parts of dry ulphate of mercury added; the whole is boiled for 15 minutes, and filtered ot from the oxide of iron, which separates. The solution, on cooling,

deposits the new salt in crystals. Cyanide of mercury forms white, translucent prisms, much resembling those of corrosive sublimate; it is soluble in 8 parts of cold water, and in a much smaller quantity at a higher temperature, and also in alcohol. The solution has a disagreeable, metalic taste, is very poisonous, and is not precipitated by alkalis. Cyanide of mercury is used in the laboratory as a source of cyanogen.

Cyanide of silver, AgCy, has been already described. *Cyanide of zinc*, ZnCy, is a white insoluble powder, prepared by mixing acetate of zinc with hydrocyanic acid. *Cyanide of cobalt*, CoCy, is obtained by similar means; it is dirty white, and insoluble. *Cyanide of palladium* forms a pale, whitish precipitate when the chloride of that metal is mixed with a soluble cyanide, including that of mercury. *Tercyanide of gold*, $AuCy_3$, is yellowish-white and insoluble, but freely dissolved by solution of cyanide of potassium. *Protocyanide of iron* has not been obtained, from the tendency of the metal to pass into the radical, and generate a *ferrocyanide*. An insoluble green compound containing $FeCy,F_4Cy_3$ was formed by M. Pelouze by passing chlorine gas into a boiling solution of ferrocyanide of potassium.

Cyanic and cyanuric acids.—These are two remarkable isomeric bodies, related in a very close and intimate manner, and presenting phenomena of great interest. Cyanic acid is the true oxide of cyanogen: it is formed in conjunction with cyanide of potassium, when cyanogen gas is transmitted over heated hydrate or carbonate of potassa, or passed into a solution of the alkaline base, the reaction resembling that by which chlorate of potassa and chloride of potassium are generated when the oxide and the salt-radical are presented to each other. Cyanate of potassa is, moreover, formed when the cyanide is exposed to a high temperature with access of air; unlike the chlorate, it bears a full red-heat without decomposition.

Hydrated Cyanic Acid, CyO,HO, is procured by heating to dull redness in a hard glass retort connected with a receiver cooled by ice, cyanuric acid, deprived of its water of crystallization. The cyanuric acid is resolved, without any other product, into hydrated cyanic acid, which condenses in the receiver to a limpid, colourless liquid, of exceedingly pungent and penetrating odour, like that of the strongest acetic acid; it even blisters the skin. When mixed with water, it decomposes almost immediately, giving rise to bicarbonate of ammonia.

$$C_2NO,HO+2HO=C_2O_4+NH_3.$$

This is the reason why the hydrated acid cannot be separated from a cyanate by a stronger acid. A trace of cyanic acid, however, always escapes decomposition, and communicates to the carbonic acid evolved a pungent smell similar to that of the sulphurous acid. The cyanates may be easily distinguished by this smell, and by the simultaneous formation of an ammonia-salt, which remains behind.

The pure hydrated cyanic acid cannot be preserved; shortly after its preparation it changes spontaneously, with sudden elevation of temperature, into a solid, white, opaque, amorphous substance, called *cyamelide*. This curious body has the same composition as hydrated cyanic acid; it is insoluble in water, alcohol, ether, and dilute acids; it dissolves in strong oil of vitriol by the aid of heat, with evolution of carbonic acid and production of ammonia; boiled with solution of caustic alkali, it dissolves, ammonia is disengaged, and a mixture of cyanate and cyanurate of the base generated. By dry distillation it is again converted into the hydrate of cyanic acid.

Cyanate of potassa, KO,CyO. — The best method of preparing this salt, is, according to Liebig, to oxidize cyanide of potassium by means of litharge. The cyanide, already containing a portion of cyanate, described p. 425, is re-melted in an earthen crucible, and finely powdered protoxide of lead added

iall portions; the oxide is instantaneously reduced, and the metal, at n a state of minute division, ultimately collects to a fused globule at the m of the crucible. The salt is poured out, and, when cold, powdered oiled with alcohol; the hot filtered solution deposits crystals of cyanate assa on cooling. The great de-oxidizing power exerted by cyanide of sium at a high temperature promises to render it a valuable agent in of the finer metallurgic operations.

other method of preparing the cyanide is to mix dried and finely-pow- ferrocyanide of potassium with half its weight of equally dry binoxide inganese; to heat this mixture in a shallow iron ladle with free expo- to air and frequent stirring until the tinder-like combustion is at an end, o boil the residue in alcohol, which extracts the cyanate of potassa.

is salt crystallizes from alcohol in thin, colourless, transparent plates, i suffer no change in dry air, but on exposure to moisture become gra- y converted, without much alteration of appearance, into bicarbonate tassa, ammonia being at the same time disengaged. Water dissolves the ite of potassa in large quantity; the solution is slowly decomposed in old, and rapidly at a boiling heat, into bicarbonate of potassa and am- a. When a concentrated solution is mixed with a small quantity of mineral acid, a precipitate falls, which consists of acid cyanurate of sa. Cyanate of potassa is reduced to cyanide of potassium by ignition charcoal in a covered crucible.

anate of potassa, mixed with solutions of lead and silver, gives rise to ible cyanates of the oxides of those metals, which are white.

ANATE OF AMMONIA; UREA. — When the vapour of hydrated cyanic acid xed with excess of ammoniacal gas, a white, crystalline, solid substance oduced, which has all the characters of a true, although not neutral, ite of ammonia. It dissolves in water, and, if mixed with an acid, evolves nic acid gas; with an alkali, it yields ammonia. If the solution be d, or if the crystals be merely exposed a certain time to the air, a por- of ammonia is dissipated, and the properties of the compound completely ged. It may now be mixed with acids without the least symptoms of nposition, while cold caustic alkali, on the other hand, fails to discharge mallest trace of ammonia. The result of this curious metamorphosis of yanate is a substance called *urea*, a product of the animal body, the and characteristic constituent of urine. This artificial formation of one products of organic life cannot fail to possess great interest. Its dis- y is due to Prof. Wöhler. The properties of urea, and the most advan- us methods of preparing it, will be found described a few pages hence.

ANURIC ACID. — The substance called *melam*, of which farther mention e made, is dissolved by gentle heat in concentrated sulphuric acid, the ion mixed with 20 or 30 parts of water, and the whole maintained at a erature approaching the boiling-point, until the specimen of the liquid, ing tried by ammonia, no longer gives a white precipitate: several days equired. The liquid, concentrated by evaporation, deposits on cooling iric acid, which is purified by re-crystallization. Another, and perhaps er method, is to heat dry and pure urea in a flask or retort: the sub- e melts, boils, disengages ammonia in large quantity, and at length nes converted into a dirty white, solid, amorphous mass, which is impure iric acid. This is dissolved by the aid of heat in strong oil of vitriol, nitric acid added by little and little until the liquid becomes nearly rless; it is then mixed with water, and suffered to cool, whereupon the iric acid separates. The urea may likewise be decomposed very con- ntly by gently heating it in a tube, while dry chlorine gas passes over i mixture of cyanuric acid and sal-ammoniac results, which is separated solving in water.

Cyanuric acid in a pure state forms colourless crystals, seldom of large size, derived from an oblique rhombic prism, which effloresce in a dry atmosphere from loss of water. It is very soluble in cold water, and requires 24 parts for solution at a boiling heat; it reddens litmus feebly, has no odour, and but little taste. This acid is tribasic; the crystals contain $C_6N_3O_3,3HO + 4HO$, and are easily deprived of the 4 eq. of water of crystallization. In point of stability, it offers a most remarkable contrast to its isomer, cyanic acid; it dissolves, as above indicated, in hot oil of vitriol, and even in strong nitric acid, without decomposition, and in fact crystallizes from the latter in an anhydrous state, containing $C_6N_3O_3,3HO$. Long-continued boiling with these powerful agents resolves it into ammonia and carbonic acid.

The connection between cyanic acid, urea, and cyanuric acid may be thus recapitulated:—

Cyanate of ammonia is converted by heat into urea.

Urea is decomposed by the same means into cyanuric acid and urea.

Cyanuric acid is changed by a very high temperature into hydrated cyanic acid.

In the latter reaction, 1 eq. of hydrated cyanuric acid splits into 3 eq. hydrated cyanic acid.

$$C_6N_3O_3,3HO = 3(C_2NO,HO).$$

Cyanate and cyanurate of oxide of ethyl. —If a dry mixture of cyanate of potassa and sulphovinate of potassa be distilled, a product is obtained which consists of a mixture of the above ethers. They are separated without difficulty, the cyanate boiling at 140° (60°C), while the boiling point of the cyanurate is much higher, namely, 528°·8 (276°C). Cyanate of ethyl is a mobile liquid, the vapour of which excites a flow of tears. The composition of cyanate of ethyl is $C_6H_5NO_2 = C_4H_5O,C_2NO = AeO,CyO$. The formation is represented by the equation $KO,CyO + KO,AeO,2SO_3 = AeO,CyO + 2(KO,SO_3)$. The cyanurate of ethyl contains $3AeO,C_6N_3O_3$; it arises in this reaction from the coalescence of 3 eq. of cyanate of ethyl. It may be likewise obtained by distilling a mixture of sulphovinate of potassa with cyanurate of potassa. Cyanurate of ethyl is a crystalline mass, slightly soluble in water, readily soluble in alcohol and ether, fusing at 185° (85°C). By substituting for sulphovinate of potassa, salts of sulphomethylic and sulphamylic acid, the corresponding methyl- and amyl-compounds may be obtained.

The study of the cyanic and cyanuric ethers, which were discovered by Wurtz, has led to very important results, which will be fully described in the section on the organic bases.

Fulminic acid.—This remarkable compound, which is isomeric both with cyanic and cyanuric acids, originates in the peculiar action exercised by nitrous acid upon alcohol in presence of a salt of silver or mercury. Neither absolute fulminic acid nor its hydrate has ever been obtained.

Fulminate of silver is prepared by dissolving 40 or 50 grains of silver, which need not be pure, in ½ oz. by measure of nitric acid of sp. gr. 1·37 or thereabouts, by the aid of a little heat; a sixpence answers the purpose very well. To the highly acid solution, while still hot, 2 measured ounces of alcohol are added, and heat applied until reaction commences. The nitric acid oxidizes part of the alcohol to aldehyde and oxalic acid, becoming itself reduced to nitrous acid, which in turn acts upon the alcohol in such a manner as to form nitrous ether, fulminic acid, and water. 1 eq. nitrous ether and 1 eq. of nitrous acid containing the elements of 1 eq. fulminic acid and 5 eq. water.

$$C_4H_5O,NO_3 + NO_3 = C_4N_2O_2 + 5HO.$$

The fulminate of silver slowly separates from the hot liquid in the form of small, brilliant, white, crystalline plates, which may be washed with a little cold water, distributed upon separate pieces of filter-paper in portions not exceeding a grain or two each, and left to dry in a warm place. When dry, the papers are folded up and preserved in a box or bottle. This is the only safe method of keeping the salt. Fulminate of silver is soluble in 36 parts of boiling water, but the greater part crystallizes out on cooling; it is one of the most dangerous substances to handle that chemistry presents; it explodes when strongly heated, or when rubbed or struck with a hard body, or when touched with concentrated sulphuric acid, with a degree of violence almost indescribable; the metal is reduced, and a large volume of gaseous matter suddenly liberated. Strange to say, it may, when very cautiously mixed with oxide of copper, be burned in a tube with as much facility as any other organic substance. Its composition thus determined is expressed in the formula $2AgO,C_4N_2O_2$.

The acid is evidently bibasic; when fulminate of silver is digested with caustic potassa, one-half of the oxide is precipitated, and a compound produced containing $AgO,KO,C_4N_2O_2$, which resembles the neutral silver-salt, and detonates by a blow. Corresponding compounds containing soda and oxide of ammonium exist; but a pure fulminate of an alkaline metal has never been formed. If fulminate of silver be digested with water and copper, or zinc, the silver is entirely displaced, and a fulminate of the new metal produced. The zinc-salt mixed with baryta-water gives rise to a precipitate of oxide of zinc, while *fulminate of zinc and baryta*, $ZnO,BaO,C_4N_2O_2$, remains in solution. *Fulminate of mercury* is prepared by a process very similar to that by which the silver-salt is obtained; one part of mercury is dissolved in 12 parts of nitric acid, and the solution mixed with an equal quantity of alcohol; gentle heat is applied, and if the reaction becomes too violent, it may be moderated by the addition from time to time of more spirit, much carbonic acid, nitrogen, and red vapours are disengaged, together with a large quantity of nitrous ether and aldehyde; these are sometimes condensed and collected for sale, but are said to contain hydrocyanic acid. The fulminate of mercury separates from the hot liquid, and after cooling may be purified from an admixture of reduced metal by solution in boiling water and re-crystallization. It much resembles the silver-salt in appearance, properties, and degree of solubility, and contains $2Hg_2O,C_4N_2O_2$. It explodes violently by friction or percussion, but, unlike the silver-com. pound, merely burns with a sudden and almost noiseless flash when kindled in the open air. It is manufactured on a large scale for the purpose of charging *percussion-caps;* sulphur and chlorate of potassa, or more frequently nitre, are added, and the powder, pressed into the cap, is secured by a drop of varnish.

The relations of composition between the three isomeric acids are beautifully seen by comparing their silver-salts; the first acid is monobasic, the second bibasic, and the third tribasic.

Cyanate of silver	$AgO\ ,\ C_2N\ O.$
Fulminate of silver	$2AgO\ ,\ C_4N_2O_2.$
Cyanurate of silver	$3AgO\ ,\ C_6N_3O_3.$

Until quite recently, beyond the accidental one of identity of composition, no relation existed between fulminic acid and its isomers. Mr. Gladstone has, however, shown that, when a solution of fulminate of copper is mixed with excess of ammonia, filtered, treated with sulphuretted hydrogen in excess, and again filtered from the insoluble sulphide of copper, the liquid obtained is a *mixed solution* of urea and sulphocyanide of ammonium.

Chlorides of cyanogen. — Chlorine forms two compounds with cyanogen

or its elements, which are isomeric, and correspond to cyanic and cyanuric acids. *Gaseous chloride of cyanogen*, CyCl, is formed by conducting chlorine gas into strong hydrocyanic acid, or by passing chlorine over moist cyanide of mercury contained in a tube sheltered from the light. It is a permanent and colourless gas at the temperature of the air, of insupportable pungency, and soluble to a very considerable extent in water, alcohol, and ether. At 0° (—17°·8C) it congeals to a mass of colourless crystals, which at 5° (—15°C) melt to a liquid whose boiling-point is 11° (—11°·6C). At the temperature of the air it is condensed to the liquid form under a pressure of four atmospheres, and when long preserved in this condition in hermetically sealed tubes it gradually passes into the solid modification. *Solid chloride of cyanogen* is generated when anhydrous hydrocyanic acid is put into a vessel of chlorine gas, and the whole exposed to the sun; hydrochloric acid is formed at the same time. It forms long colourless needles, which exhale a powerful and offensive odour, compared by some to that of the excrement of mice; it melts at 284° (140°C), and sublimes unchanged at a higher temperature. When heated in contact with water, it is decomposed into cyanuric and hydrochloric acids. This compound may be represented by the formula Cy_3Cl_3, or $C_6N_3Cl_3$. It dissolves in alcohol and ether without decomposition.

BROMIDE AND IODIDE OF CYANOGEN correspond to the first of the preceding compounds, and are prepared by distilling bromine or iodine with cyanide of mercury. They are colourless, volatile, solid substances, of powerful odour.

FERROCYANOGEN AND ITS COMPOUNDS.

When a solution of cyanide of potassium is digested with iron-filings at a gentle heat in an open vessel, oxygen is absorbed from the air, the iron dissolves quietly and disappears, and a highly alkaline, yellow liquid is obtained, which on evaporation deposits lemon-yellow crystals containing potassium in combination with a new salt-radical composed of the metal iron and the elements of cyanogen; in the mother-liquid hydrate of potassa is found. 3 eq. cyanide of potassium, 1 eq. iron, and 1 eq. oxygen, yield 1 eq. of the new salt, and 1 eq. of potassa.

$$3KCy + Fe + O = KO + K_2,C_6N_3Fe.$$

The new substance is called *ferrocyanogen*, and is designated by the symbol Cfy; it is bibasic, neutralizing 2 equivalents of metal or hydrogen, and contains *the elements of* 3 equivalents of cyanogen combined with 1 eq. of iron. It has never been isolated.

When iron in filings is heated in a small retort with a solution of cyanide of potassium, it is dissolved with evolution of hydrogen, caustic potassa and the new substance being generated; the oxygen in this case is derived from the decomposition of water. Sulphide of iron and cyanide of potassium give rise, under similar circumstances, to sulphide of potassium and ferrocyanide of potassium.

HYDROFERROCYANIC ACID, Cfy2H. — Ferrocyanide of lead or copper, both of which are insoluble, may be suspended in water, and decomposed by a stream of sulphuretted hydrogen gas. The filtered solution, evaporated in the vacuum of the air-pump over a surface of oil of vitriol, furnishes the acid in a solid form. If the aqueous solution be agitated with ether, nearly the whole of the acid separates in colourless, crystalline laminæ; it may even be made in large quantity by adding hydrochloric acid to a strong solution of ferrocyanide of potassium in water free from air, and shaking the whole with ether. The crystals may be dissolved in alcohol, and the acid again thrown down by ether, which possesses the remarkable property of precipitating this substance from solution. Hydroferrocyanic acid differs completely

from hydrocyanic acid; its solution in water has a powerfully acid taste and reaction, and decomposes alkaline carbonates with effervescence; it refuses to dissolve oxide of mercury in the cold, but when heat is applied, undergoes decomposition, forming cyanide of mercury and a peculiar compound of iron, cyanogen, and oxygen, with reduction of some of the oxide. In a dry state the acid is very permanent, but when long exposed to the air in contact with water it becomes entirely converted into Prussian blue. This interesting substance was discovered by Mr. Porrett.

Ferrocyanide of potassium, frequently called *Yellow prussiate of potash*, $K_2Cfy+3HO$, or $K_2C_6N_3Fe+3HO$.—This most beautiful salt is manufactured on a large scale by the following process, which will now be easily intelligible:—Dry refuse animal matter of any kind is fused at a red-heat with impure carbonate of potassa and some iron-filings in a large iron vessel, from which the air should be excluded as much as possible; cyanide of potassium is generated in large quantity. The melted mass is afterwards treated with hot water, which dissolves out the cyanide and other salts; the cyanide being quickly converted by the oxide or sulphide[1] of iron into ferrocyanide. The filtered solution is evaporated, and the first-formed crystals purified by re-solution. If a sufficient quantity of iron be not present, great loss is incurred by the decomposition of the cyanide into formate of potassa and ammonia.

Ferrocyanide of potassium forms large, transparent, yellow crystals, derived from an octahedron with a square base; they cleave with facility in a direction parallel to the base of the octahedron, and are tough and difficult to powder. They dissolve in 4 parts of cold, and in 2 of boiling water, and are insoluble in alcohol. They are permanent in the air, and have a mild saline taste. The salt has no poisonous properties, and in small doses, at least, is merely purgative. Exposed to a gentle heat, it loses 3 eq. of water, and becomes anhydrous; at a high temperature it yields cyanide of potassium, carbide of iron, and various gaseous products; if air be admitted, the cyanide becomes cyanate.

The ferrocyanides are often described as double salts in which protocyanide of iron is combined with other metallic cyanides, or with hydrogen. Thus, hydroferrocyanic acid is written FeCy,2HCy, and ferrocyanide of potassium, FeCy,2KCy+3HO; the oxygen and hydrogen of the water of crystallization being respectively adequate to convert the metals into protoxide and the cyanogen into hydrocyanic acid. This view has the merit of simplicity, and will often prove an useful aid to the memory, but there are insuperable objections to its adoption as a sound and satisfactory theory.

Ferrocyanide of potassium is a chemical reagent of great value; when mixed in solution with neutral or slightly acid salts of the metals proper, it gives rise to precipitates which very frequently present highly characteristic colours. In most of these compounds the potassium of the base is simply displaced by the new metal: the beautiful brown ferrocyanide of copper contains, for example, Cu_2Cfy or $Cu_2C_6N_3Fe$, and that of lead, Pb_2Cfy. With salts of protoxide of iron it gives a bluish precipitate, which becomes rapidly dark blue by exposure to air; this appears to be a compound of the neutral ferrocyanide of iron, Fe_2Cfy, with ferrocyanide of potassium.

When a ferrocyanide is added to a solution of salt of sesquioxide of iron, *Prussian blue* is produced. Although this remarkable substance has now been long known, and many elaborate researches have been made with a view of determining its exact composition, the problem cannot yet be said to be completely solved. This difficulty arises in great measure from the existence of several distinct deep blue compounds formed under different cir-

[1] *The sulphur is derived from the* reduced sulphate of the crude pearl-ashes used in this *manufacture.*

cumstances, and having many properties in common, which have been frequently confounded. The following is a summary of the account given by Berzelius, who has paid much attention to this subject.

Ordinary Prussian Blue, $C_{18}N_9Fe_7$, or Fe_4Cfy_3. — This is best prepared by adding nitrate of sesquioxide of iron to solution of ferrocyanide of potassium, keeping the latter in slight excess. It forms a bulky precipitate of the most intense blue, which shrinks to a comparatively small compass when well washed and dried by gentle heat. In a dry state it is hard and brittle, much resembling in appearance the best indigo; the fresh-fractured surfaces have a beautiful copper-red lustre, similar to that produced by rubbing indigo with a hard body. Prussian blue is quite insoluble in water and dilute acids, with the exception of oxalic acid, in a solution of which it dissolves, forming a deep blue liquid, which is sometimes used as ink; concentrated oil of vitriol converts it into a white, pasty mass, which again becomes blue on the addition of water. Alkalis destroy the colour instantly; they dissolve out a ferrocyanide, and leave sesquioxide of iron. Boiled with water and red oxide of mercury, it yields a cyanide of the metal, and sesquioxide of iron. Heated in the air, Prussian blue burns like tinder, leaving a residue of sesquioxide of iron. Exposed to a high temperature in a close vessel, it disengages water, cyanide of ammonium, and carbonate of ammonia, and leaves carbide of iron. This substance forms a very beautiful pigment, both in oil and a water-colour, but has little permanency. The Prussian blue of commerce is always exceedingly impure; it contains alumina and other matters, which greatly diminish the brilliancy of the colour.

The production of Prussian blue by mixing sesquioxide salts of iron and ferrocyanide of potassium or sodium may thus be elucidated:—

3 eq. ferrocyanide potassium	3 eq. ferrocyanogen 6 eq. potassium	Prussian blue.
2 eq. nitrate of sesquioxide of iron	4 eq. iron 6 eq. oxygen 6 eq. nitric acid	6 eq. nitrate of potassa.

In the above formula no account is taken of the elements of water which Prussian blue certainly contains; in fact it must be looked upon as still requiring examination.

The theory of the beautiful test of Scheele for the discovery of hydrocyanic acid, or any soluble cyanide, will now be clearly intelligible. The liquid is mixed with a salt of protoxide of iron and excess of caustic alkali; the protoxide of iron quickly converts the alkaline cyanide into ferrocyanide. By exposure for a short time to the air, another portion of the hydrated oxide becomes peroxidized; when excess of acid is added, this is dissolved, together with the unaltered protoxide; and thus presented to the ferrocyanide in a state fitted for the production of Prussian blue.

Basic Prussian Blue, $Fe_4Cfy_3 + Fe_2O_3$. — This is a combination of Prussian blue with sesquioxide of iron; it is formed by exposing to the air the white or pale blue precipitate caused by a ferrocyanide in a solution of protosalt of iron. It differs from the preceding in being soluble in pure water, although not in a saline solution.

The blue precipitate obtained by adding nitrate of sesquioxide of iron to a large excess of ferrocyanide of potassium, is a mixture of insoluble Prussian blue with a compound containing that substance in union with ferrocyanide of potassium, or $Fe_4Cfy_3 + 2K_2Cfy$. This also dissolves in water as soon as the salts have been removed by washing.

he other ferrocyanides may be despatched in a few words.

he *soda-salt*, $Na_2Cfy + 12HO$, crystallizes in yellow four-sided prisms, :h are efflorescent in the air and very soluble.

errocyanide of ammonium, $(NH_4)C_2fy + 3HO$, is isomorphous with ferro-iide of potassium; it is easily soluble, and is decomposed by ebullition. *ocyanide of barium*, Ba_2Cfy, prepared by double decomposition, or by ng Prussian blue in baryta-water, forms minute yellow, anhydrous crys-which have but a small degree of solubility even in boiling water. The esponding compounds of *strontium*, *calcium*, and *magnesium*, are more ly soluble. The ferrocyanides of *silver*, *lead*, *zinc*, *manganese*, and *bis-*t are white and insoluble; those of *nickel* and *cobalt* are pale green, and luble; and, lastly, that of *copper* has a beautiful reddish-brown tint.

errocyanides with two basic metals are occasionally met with; when, for nple, concentrated solutions of chloride of calcium and ferrocyanide of issium are mixed, a sparingly-soluble crystalline precipitate falls, con-ing KCaCfy, the salt-radical being half saturated with potassium, and ' with calcium; many similar compounds have been formed.

ERRI-, OR FERRIDCYANOGEN, $C_{12}N_6Fe_2$; or Cfdy. — This name is given to ibstance, by some thought to be a new salt-radical, isomeric with ferro-nogen, but differing in capacity of saturation; it has never been isolated. *ricyanide of potassium* is thus prepared:—Chlorine is slowly passed, with ation, into a somewhat dilute and cold solution of ferrocyanide of potas-n, until the liquid acquires a deep reddish-green colour, and ceases to dpitate a salt of the sesquioxide of iron. It is then evaporated until a i begins to form upon the surface, filtered, and left to cool; the salt is ified by re-crystallization. It forms regular prismatic, or sometimes ilar crystals, of a beautiful ruby-red tint, permanent in the air, and solu-in 4 parts of cold water; the solution has a dark greenish colour. The tals burn when introduced into the flame of a candle, and emit sparks. erricyanide of potassium contains K_3Cfdy; hence the radical is tribasic; salt is formed by the abstraction of an equivalent of potassium from 2 of the yellow ferrocyanide of potassium. It is decomposed by excess hlorine, and by deoxidizing agents, as sulphuretted hydrogen. The : *red prussiate of potash* is often, but very improperly, given to this sub-ce.

erricyanide of hydrogen is obtained in the form of a reddish-brown acid d, by decomposing ferricyanide of lead with sulphuric acid; it is very ible, and is resolved, by boiling, into a hydrated sesquicyanide of iron, isoluble dark green powder, containing $Fe_2Cy_3 + 3HO$, and hydrocyanic The ferricyanides of *sodium*, *ammonium*, and of the alkaline earths, ioluble; those of most of the other metals are insoluble. Ferricyanide otassium, added to a salt of the *sesquioxide* of iron, occasions no precipi-but merely a darkening of the reddish-brown colour of the solution; protoxide of iron, on the other hand, it gives a deep blue precipitate, aining Fe_3Cfdy, which, when dry, has a brighter tint than that of Prus-blue; it is known under the name of *Turnbull's blue*. Hence, ferri-ide of potassium is as excellent a test for protoxide of iron, as the yellow cyanide is for the sesquioxide.

BALTOCYANOGEN. — A series of compounds analogous to the preceding, aining cobalt in place of iron, have been formed and studied; a hydro-acid has been obtained and a number of salts, which much resemble of ferricyanogen. Several other metals of the same isomorphous ly are found capable of replacing iron in these circumstances.

TROPRUSSIDES.—The action of nitric acid upon ferrocyanides and ferri-ides gives rise to the formation of a very interesting series of new salts, h were discovered by Dr. Playfair. The general formula of these salts

... and having many properties in common, which ... The following is a summary of the ... much attention to this subject.

... $C_{12}N_6Fe_7$ or Fe_7Cfy_3. — This ... of iron to solution of ... the latter in slight excess. It forms ... which shrinks to a comp... water, and dried by gentle heat. In ... in appearance the best ... a beautiful copper-red lustre, ... with a hard body. Prussian ... of ... acids, with the exception of oxali... ...rogen, ... forming a deep blue liquid, which ... the nit... converts it into ... by tre... on the addition of water ... nitric aci... dissolve out a ferrocyani... solution, after the ... with water and red oxide of ... until salts of pro... and ... oxide of iron. Her... precipitate. The ... leaving a residue of ... and occasionally ... in a close vessel, it ... with carbonate of soda ... ammonia, and ... a ruby-coloured ... a very beautiful pigment, ... of nitrate of potassa and ... permanency. The Prussia... of the latter are ... alumina or ... and of a splendid ... of the colour. ... most beautiful violet ... by Dr. Playfair as ...

The production of Prussian ... ferrocyanide of potassium ...

... COMPOUNDS AND DERIVAT...

... combine with sulphur, forming a ... called *sulphocyanogen*, which ... represented by the symbol Csy.

... Yellow ferrocyanide ... crystallization, is intimately mixed wi... whole heated to tranquil fusion ... When cold, the melted ma... a mixture of sulphocyanide of pota... heated but the excess of ... oxide of iron, is mixed with carbonate of ... and potassium substituted ... as far as possible ... The ... over an open fire ... a small bulk. ... crystals are drained, purified by re... them, spread on filter-paper, ov...

... the elements of the ye... of ferrocyanide of potassium, and 6 eq. ... of potassium and ... eq. of sulpho...

$... = 2\,K\,C_2NS_2 + Fe\,C_2NS_2$

... simpler process consists in gradually heat... a mixture of 46 parts of dried ferro...

f pure carbonate of potassa. The mass is
tion evaporated to dryness and ex-
nosits splendid crystals on cool-

less prisms, or plates,
and is destitute of poi-
. alcohol, and deliquesces
ed, it fuses to a colourless
n.
on of sulphocyanide of potas-
ow, insoluble substance, resem-
produced, together with chloride
tube delivering the gas; the liquid
d disengages a pungent vapour, pro-
ow matter may be collected on a filter,
dried: it retains its brilliancy of tint.
rally been applied to this substance, from
dical of the sulphocyanides; it is, however,
th oxygen and hydrogen, and a formula much
nging to the true sulphocyanogen, namely C_8H_2
gned to it. The yellow substance is quite insoluble
ther; it dissolves in concentrated sulphuric acid,
tated by dilution. Caustic potassa also dissolves it,
acids throw down from this solution a pale yellow,
ing acid properties. When heated in a dry state, the
anogen evolves sulphur and bisulphide of carbon, and
pale straw-yellow substance, called *mellon*, which contains
n to combine with hydrogen and the metals. Mellon bears
ithout decomposition, but is resolved by strong ignition into
nogen and nitrogen gases. It is quite insoluble in water,
te acids.

YANIC ACID, HCsy, is obtained by decomposing sulphocya-
spended in water, by sulphuretted hydrogen. The filtered
less, very acid, and not poisonous; it is easily decomposed,
x manner, by ebullition; and by exposure to the air. By
liquid with ammonia, and evaporating very gently, to dry-
de of ammonium, NH_4Csy, is obtained as a deliquescent,
is salt may be conveniently prepared by digesting hydro-
yellow sulphide of ammonium, and boiling off the excess of
$S_3+HCy=NH_4Csy+HS$). The sulphocyanides of *sodium*,
, *calcium*, *manganese*, and *iron* are colourless, and very
lead and *silver* are white and insoluble. A soluble sulpho-
ith a salt of the sesquioxide of iron, gives no precipitate
quid to assume a deep blood-red tint, exactly similar to that
ilar circumstances by meconic acid; hence the occasional
nide of potassium as a test for iron in the state of sesqui-
t facility with which hydrocyanic acid may be converted
le of ammonium enables us to ascertain the presence by the
cribed. The cyanide to be examined is mixed in a watch-
hydrochloric acid and covered with another watch-glass, to
s of yellow sulphide of ammonium adhere. On heating the
anic acid is disengaged, which combines with the sulphide
nd produces sulphocyanide of ammonium; this, after the
excess of sulphide, yields the red colour with solution of
on.

N.—A series of salts containing selenium, and corresponding

appears to be $M_2Fe_2Cy_5NO$, which exhibits a close relation with those of the ferro- and ferricyanides.

$$2M_2Cfy = M_4\ Fe_2\ Cy_6 = \text{ferrocyanides.}$$
$$M_3\ Fe_2\ Cy_6 = \text{ferricyanides.}$$
$$M_2\ Fe_2\left\{\begin{matrix}Cy_5\\NO\end{matrix}\right. = \text{nitroprussides.}$$

According to this formula, the formation of the nitroprusside would consist in the reduction of the nitric acid to the state of protoxide of nitrogen, which replaces 1 eq. of cyanogen in 2 eq. of ferrocyanide. The formation of these salts is attended by the production of a variety of secondary products, such as cyanogen, oxamide, hydrocyanic acid, nitrogen, carbonic acid, &c. One of the finest compounds of this series is the nitroprusside of sodium, $Na_2,FeCy_5NO+4HO$, which is readily obtained by treating 2 parts of the powdered ferrocyanide with 5 parts of common nitric acid, previously diluted with its own volume of water. The solution, after the evolution of gas has ceased, is digested on the water-bath, until salts of protoxide of iron no longer yield a blue but a slate-coloured precipitate. The liquid is allowed to cool, when much nitrate of potassa, and occasionally oxamide, is deposited; it is filtered and neutralized with carbonate of soda, which yields a green or brown precipitate, and furnishes a ruby-coloured filtrate. This, on evaporation, gives a crystallization of nitrate of potassa and soda, together with the new salt. The crystals of the latter are selected and purified by crystallization; they are rhombic, and of a splendid ruby colour. The soluble nitroprussides strike a most beautiful violet tint with soluble sulphides. This reaction is recommended by Dr. Playfair as the most delicate test for alkaline sulphides.

SULPHOCYANOGEN, ITS COMPOUNDS AND DERIVATIVES.

The elements of cyanogen combine with sulphur, forming a very important and well-defined salt-radical, called *sulphocyanogen*, which contains C_2NS_2, and is monobasic; it is expressed by the symbol Csy.

SULPHOCYANIDE OF POTASSIUM, KCsy. — Yellow ferrocyanide of potassium, deprived of its water of crystallization, is intimately mixed with half its weight of sulphur, and the whole heated to tranquil fusion in an iron pot, and kept some time in that condition. When cold, the melted mass is boiled with water, which dissolves out a mixture of sulphocyanide of potassium and sulphocyanide of iron, leaving little behind but the excess of sulphur employed in the experiment. This solution, which becomes red on exposure to the air from the oxidation of the iron, is mixed with carbonate of potassa, by which the oxide of iron is precipitated, and potassium substituted; an excess of the carbonate must be, as far as possible, avoided. The filtered liquid is concentrated, by evaporation over an open fire, to a small bulk, and left to cool and crystallize. The crystals are drained, purified by re-solution if necessary, or dried by inclosing them, spread on filter-paper, over a surface of oil of vitriol, covered by a bell-jar.

The reaction between the sulphur and the elements of the yellow salt is easily explained: 1 eq. of ferrocyanide of potassium, and 6 eq. sulphur, yielded 2 eq. of sulphocyanide of potassium, and 1 eq. of sulphocyanide of iron.

$$K_2Cfy = C_6N_3Fe,K_2 + 6S = 2(KC_2NS_2) + FeC_2NS_2.$$

Another and perhaps simpler process consists in gradually heating to redness in a covered vessel a mixture of 46 parts of dried ferrocyanide

potassium, 32 of sulphur, and 17 of pure carbonate of potassa. The mass is exhausted by water, the aqueous solution evaporated to dryness and extracted with alcohol. The alcoholic liquid deposits splendid crystals on cooling or evaporation.

The new salt crystallizes in long, slender, colourless prisms, or plates, which are anhydrous; it has a bitter, saline taste, and is destitute of poisonous properties; it is very soluble in water and alcohol, and deliquesces when exposed to a moist atmosphere. When heated, it fuses to a colourless liquid, at a temperature far below that of ignition.

When chlorine is passed into a strong solution of sulphocyanide of potassium, a large quantity of a bulky, deep yellow, insoluble substance, resembling some varieties of chromate of lead, is produced, together with chloride of potassium, which tends to choke up the tube delivering the gas; the liquid sometimes assumes a deep red tint, and disengages a pungent vapour, probably chloride of cyanogen. This yellow matter may be collected on a filter, well washed with boiling water, and dried: it retains its brilliancy of tint. The term *sulphocyanogen* has generally been applied to this substance, from its supposed identity with the radical of the sulphocyanides; it is, however, invariably found to contain both oxygen and hydrogen, and a formula much more complex than that belonging to the true sulphocyanogen, namely $C_8H_2N_4S_8O$, has been lately assigned to it. The yellow substance is quite insoluble in water, alcohol, and ether; it dissolves in concentrated sulphuric acid, from which it is precipitated by dilution. Caustic potassa also dissolves it, with decomposition; acids throw down from this solution a pale yellow, insoluble body, having acid properties. When heated in a dry state, the so-called sulphocyanogen evolves sulphur and bisulphide of carbon, and leaves a curious, pale straw-yellow substance, called *mellon*, which contains C_6N_4, and is known to combine with hydrogen and the metals. Mellon bears a dull red-heat without decomposition, but is resolved by strong ignition into a mixture of cyanogen and nitrogen gases. It is quite insoluble in water, alcohol, and dilute acids.

Hydrosulphocyanic acid, HCsy, is obtained by decomposing sulphocyanide of lead, suspended in water, by sulphuretted hydrogen. The filtered solution is colourless, very acid, and not poisonous; it is easily decomposed, in a very complex manner, by ebullition; and by exposure to the air. By neutralizing the liquid with ammonia, and evaporating very gently, to dryness, *sulphocyanide of ammonium*, NH_4Csy, is obtained as a deliquescent, saline mass. This salt may be conveniently prepared by digesting hydrocyanic acid with yellow sulphide of ammonium, and boiling off the excess of the latter ($NH_4S_3+HCy=NH_4Csy+HS$). The sulphocyanides of *sodium*, *barium*, *strontium*, *calcium*, *manganese*, and *iron* are colourless, and very soluble; those of *lead* and *silver* are white and insoluble. A soluble sulphocyanide, mixed with a salt of the sesquioxide of iron, gives no precipitate but causes the liquid to assume a deep blood-red tint, exactly similar to that caused under similar circumstances by meconic acid; hence the occasional use of sulphocyanide of potassium as a test for iron in the state of sesquioxide. The great facility with which hydrocyanic acid may be converted into sulphocyanide of ammonium enables us to ascertain the presence by the iron-test just described. The cyanide to be examined is mixed in a watch-glass with some hydrochloric acid and covered with another watch-glass, to which a few drops of yellow sulphide of ammonium adhere. On heating the mixture, hydrocyanic acid is disengaged, which combines with the sulphide of ammonium, and produces sulphocyanide of ammonium; this, after the expulsion of the excess of sulphide, yields the red colour with solution of sesquioxide of iron.

Selenocyanogen.—A series of salts containing selenium, and corresponding

in their composition and properties with sulphocyanides, exist. They have been lately studied by Mr. Crookes.

Melam. — Such is the name given by Liebig to a curious buff-coloured, insoluble, amorphous substance, obtained by the distillation at a high temperature of sulphocyanide of ammonium. It may be prepared in large quantity by intimately mixing 1 part of perfectly dry sulphocyanide of potassium with 2 parts of powdered sal-ammoniac, and heating the mixture for some time in a retort or flask; bisulphide of carbon, sulphide of ammonium, and sulphuretted hydrogen are disengaged and volatilised, while a mixture of melam, chloride of potassium, and some sal-ammoniac remains; the two latter substances are removed by washing with hot water. Melam contains $C_{12}H_9N_{11}$; it dissolves in concentrated sulphuric acid, and gives, by dilution with water and long boiling, cyanuric acid. The same substance is produced with disengagement of ammonia when melam is fused with hydrate of potassa. When strongly heated, melam is resolved into mellon and ammonia.

If melam be boiled for a long time in a moderately strong solution of caustic potassa, until the whole has dissolved, and the liquid be then concentrated, a crystalline substance separates on cooling, which is called melamine. By re-crystallization it is obtained in colourless crystals, having the figure of an octahedron with rhombic base; it is but slightly soluble in cold water, fusible by heat, and volatile with trifling decomposition. It contains $C_6H_6N_6$, and acts as a base, combining with acids to crystallizable compounds. A second basic substance called *ammeline*, very similar in properties to melamine, is found in the alkaline mother-liquor from which the melamine has separated; it is thrown down on neutralizing the liquid with acetic acid. The precipitate, dissolved in dilute nitric acid, yields crystals of nitrate of ammeline, from which the pure ammeline may be separated by ammonia. It forms a brilliant white powder of minute needles, insoluble in water and alcohol, and contains $C_6H_5N_5O_2$. When ammeline is dissolved in concentrated sulphuric acid, and the solution mixed with a large quantity of water, or, better, spirit of wine, a white, insoluble powder falls, which is designated *ammelide*, and is found to contain $C_{12}H_9N_9O_6$. When long boiled with dilute sulphuric acid, melamine, ammeline, and ammelide are converted into cyanuric acid and ammonia.

UREA; URIC ACID AND ITS PRODUCTS.

These bodies are closely connected with the cyanogen-compounds, and may be most conveniently discussed in the present place.

Urea. — Urea may be extracted from its natural source, the urine, or it may be prepared by artificial means. Fresh urine is concentrated in a water-bath, until reduced to an eighth or a tenth of its original volume, and filtered through cloth from the insoluble deposit of urates and phosphates. The liquid is mixed with about an equal quantity of a strong solution of oxalic acid in hot water, and the whole vigorously agitated and left to cool. A very copious fawn-coloured crystalline precipitate of *oxalate of urea* is obtained, which may be placed upon a cloth filter, slightly washed with cold water, and pressed. This is to be dissolved in boiling-hot water, and powdered chalk added until effervescence ceases, and the liquid becomes neutral. The solution of urea is filtered from the insoluble oxalate of lime, warmed with a little animal charcoal, again filtered, and concentrated by evaporation, avoiding ebullition, until crystals form on cooling; these are purified by a repetition of the last part of the process. Urea can be extracted in great abundance from the urine of horses and cattle, duly concentrated, and from which the hippuric acid has been separated by the addition of hydrochloric acid; oxalic acid then throws down the oxalate in such quantity as to render

he whole semi-solid. Another process consists in precipitating the evaporated urine with concentrated nitric acid, when *nitrate of urea* is precipitated, which is re-crystallized with animal charcoal, and lastly decomposed by carbonate of baryta. A mixture of nitrate of baryta and urea is formed, which is evaporated to dryness on the water-bath, and exhausted with alcohol, from which the urea crystallizes on cooling.

By artificial means, urea is produced by heating solution of cyanate of ammonia. The following method of proceeding yields it in any quantity that can be desired. Cyanate of potassa, prepared by Liebig's process,[1] is dissolved in a small quantity of water, and a quantity of dry neutral sulphate of ammonia, equal in weight to the cyanate, added. The whole is evaporated to dryness in a water-bath, and the dry residue boiled with strong alcohol, which dissolves out the urea, leaving the sulphate of potassa and the excess of sulphate of ammonia untouched. The filtered solution, concentrated by distilling off a portion of the spirit, deposits the urea in beautiful crystals of considerable magnitude.

Urea forms transparent, colourless, four-sided prisms, which are soluble in an equal weight of cold water, and in a much smaller quantity at a high temperature. It is also readily dissolved by alcohol. It is inodorous, has a cooling, saline taste, and is permanent in the air, unless the latter be very damp. When heated, it melts, and at a higher temperature, decomposes with evolution of ammonia and cyanate of ammonia; cyanuric acid remains, which bears a much greater heat without change. The solution of urea is neutral to test-paper; it is not decomposed in the cold by alkalis or by hydrate of lime, but at a boiling heat emits ammonia, and forms a carbonate of the base. The same change happens by fusion with the alkaline hydrates. Brought into contact with nitrous acid, it is decomposed instantly into a mixture of nitrogen and carbonic acid gases; this decomposition explains the use of urea in preparing nitric ether (see page 354). With chlorine it yields hydrochloric acid, nitrogen, and carbonic acid. Crystallized urea is anhydrous; it contains $C_2H_4N_2O_2$, or the *elements of cyanate of oxide of ammonium*. It differs from carbonate of ammonia by the elements of water; hence it might with some propriety be called *carbamide*. It is easily converted into carbonate of ammonia by assimilating the oxygen and hydrogen of 2 eq. of water. A solution of pure urea shows no tendency to change by keeping, and is not decomposed by boiling: in the urine, on the other hand, where it is associated with putrefiable organic matter, as mucus, the case is different. In putrid urine no urea can be found, but enough carbonate of ammonia to cause brisk effervescence with an acid; and if urine, in a recent state, be long boiled, it gives off ammonia and carbonic acid from the same source.

Urea acts as a salt-base; with nitric acid it forms a sparingly soluble compound, which crystallizes, when pure, in small, indistinct, colourless plates, containing single equivalents of urea, nitric acid, and water. When colourless nitric acid is added to urine, concentrated to a fourth or a sixth of its volume, and cold, the nitrate crystallizes out in large, brilliant, yellow laminæ, which are very insoluble in the acid liquid. The production of this nitrate is highly characteristic of urea. The oxalate, when pure, crystallizes in large, transparent, colourless plates, which have an acid reaction, and are sparingly soluble; it contains an equivalent of water. Urea forms several compounds with metallic salts, e. g., with those of mercury. On mixing a liquid containing urea with a solution of nitrate of protoxide of mercury, a white precipitate takes place, which is a compound of urea with 1 eq. of protoxide of mercury. If the nitric acid which is thus set free, be

[1] See page 427.

neutralised by the addition of an alkali or baryta-water, the whole of the urea is removed from the liquid in the form of the above compounds. Baron Liebig, to whom we are indebted for this observation, has based upon this deportment a process of determining the amount of urea in urine. The details of this method, which is equally interesting to the chemist and the physiologist, have not yet been published.

A series of substances analogous to urea, which have lately been discovered and described under the name of methylamine-urea, ethylamine-urea, biethylamine-urea, &c., will be noticed in the section on the vegeto-alkalis.

Uric, or lithic acid.—This is a product of the animal organism, and has never been formed by artificial means. It may be prepared from human urine by concentration, and addition of hydrochloric acid; it crystallises out after some time in the form of small, reddish, translucent grains, very difficult to purify. A much preferable method is, to employ the solid white excrement of serpents, which can be easily procured; this consists almost entirely of uric acid and urate of ammonia. It is reduced to powder, and boiled in dilute solution of caustic potassa; the liquid, filtered from the insignificant residue of feculent matter, and earthy phosphates, is mixed with excess of hydrochloric acid, boiled for a few minutes, and left to cool. The product is collected on a filter, washed until free from chloride of potassium, and dried by gentle heat.

Fig. 173.

Uric acid, thus obtained, forms a glistening, snow-white powder, tasteless, inodorous, and *very* sparingly soluble. It is seen under the microscope to consist of minute, but regular crystals (fig. 173). It dissolves in concentrated sulphuric acid without apparent decomposition, and is precipitated by dilution with water. By destructive distillation, uric acid yields cyanic, hydrocyanic, and carbonic acids, carbonate of ammonia, and a black coaly residue, rich in nitrogen. By fusion with hydrate of potassa, it furnishes carbonate and cyanate of the base, and cyanide of the alkaline metal. When treated with nitric acid and with binoxide of lead, it undergoes decomposition in a manner to be presently described.

Uric acid is found by analysis to contain $C_{10}H_2N_4O_4,2HO$. It is a bibasic acid.

The only salts of uric acid that have attracted any attention are those of the alkalis; acid *urate of potassa* contains $KO,HO,C_{10}H_2N_4O_4$; it is deposited from a hot, saturated solution of uric acid in the dilute alkali as a white, sparingly soluble concrete mass, composed of minute needles; it requires about 500 parts of cold water for solution, is rather more soluble at a high temperature, and much more soluble in excess of alkali. *Urate of soda* resembles the salt of potassa; it forms the chief constituent of the gouty concretions in the joints, called *chalk-stones*. *Urate of ammonia* is also a sparingly soluble compound, requiring for the purpose about 1000 parts of cold water; the solubility is very much increased by the presence of a small quantity of certain salts, as chloride of sodium. This is the most common of the urinary deposits, forming a buff-coloured or pinkish cloud or muddiness, which disappears by re-solution when the urine is warmed; the secretion from which this is deposited has an acid reaction. It occurs also as a calculus.

The following substances result from the oxidation of uric acid by binoxide of lead and nitric acid; they are some of the most beautiful and interesting bodies known, most of which have been discovered by Liebig and Wöhler.

Allantoin.—Allantoin occurs ready formed in the allantoic liquid of the fœtal calf. It is produced artificially by boiling together water, uric acid,

and pure, freshly prepared binoxide of lead; the filtered liquid, duly concentrated by evaporation, deposits crystals of allantoin on cooling, which are purified by re-solution and the use of animal charcoal. It forms small but most brilliant prismatic crystals, which are transparent and colourless, destitute of taste, and without action on vegetable colours. Allantoin dissolves in 160 parts of cold water, and in a small quantity at the boiling temperature. It is decomposed by boiling with nitric acid, and by oil of vitriol when concentrated and hot, being in this case resolved into ammonia, carbonic acid, and carbonic oxide. Heated with concentrated solution of caustic alkalis, it is decomposed into ammonia and oxalic acid, which latter combines with the base. These reactions are explained by the analysis of the substance, which shows it to be composed of the elements of oxalate of ammonia *minus* those of three equivalents of water, or $C_4H_3N_2O_3$.

The production of allantoin from uric acid and binoxide of lead is also perfectly intelligible; 1 eq. of uric acid, 2 eq. of oxygen from the binoxide, and 3 eq. of water, contain the elements of allantoin, 2 eq. of oxalic acid, and 1 eq. of urea.

$$\left.\begin{matrix} C_{10}H_4N_4O_6+2O \\ +3HO \end{matrix}\right\} = \left\{\begin{matrix} C_4H_3N_2O_3+2(HO,C_2O_3) \\ +C_2H_4N_2O_2. \end{matrix}\right.$$

The insoluble matter from which the solution of allantoin is filtered consists in great part of oxalate of lead, and the mother-liquor from which the crystals of allantoin have separated, yields, on farther evaporation, a large quantity of pure urea.

Alloxan. — This is the characteristic product of the action of concentrated nitric acid on uric acid in the cold. An acid is prepared, of sp. gr. 1·45, or thereabouts, and placed in a shallow open basin; into this a third of its weight of dry uric acid is thrown, by small portions, with constant agitation, care being taken that the temperature never rises to any considerable extent. The uric acid at first dissolves with copious effervescence of carbonic acid and nitrogen, and eventually, the whole becomes a mass of white, crystalline, pasty matter. This is left to stand some hours, drained from the acid liquid in a funnel whose neck is stopped with powder and fragments of glass, and afterwards more effectually dried upon a porous tile. This is *alloxan* in a crude state; it is purified by solution in a small quantity of water, and crystallization.

Alloxan crystallizes with facility from a hot and concentrated solution, slowly suffered to cool, in solid, hard, anhydrous crystals of great regularity, which are transparent, nearly colourless, have a high lustre, and the figure of a modified rhombic octahedron. A cold solution, on the other hand, left to evaporate spontaneously, deposits large foliated crystals, which contain 6 eq. of water; they effloresce rapidly in the air. Alloxan is very soluble in water; the solution has an acid reaction, a disagreeable astringent taste, and stains the skin, after a time, red or purple. It is decomposed by alkalis, and both by oxidizing and de-oxidizing agents; its most characteristic property is that of forming a deep blue compound with a salt of protoxide of iron and an alkali.

Alloxan contains $C_8H_4N_2O_{10}$; its production is thus illustrated: 1 eq. of uric acid, 4 eq. of water, and 2 eq. of nitric acid, contain the elements of alloxan, 2 eq. carbonic acid, 2 eq. of free nitrogen, 1 eq. of nitrate of ammonia:—

$$\left.\begin{matrix} C_{10}H_4N_4O_6+2HO \\ +2(HO,NO_5) \end{matrix}\right\} = C_8H_4N_2O_{10}+2CO_2+N_2+NH_4O,NO_5.$$

When to a solution of alloxan, heated to 140° (60°C), baryta-water is added *as long as the precipitate first* produced re-dissolves, and the filtered solution

when this is cool, a substance is deposited in small, colourless, prismatic crystals, which consist of baryta in combination with a new acid, the alloxanic; from this salt the base may be separated by the cautious addition of dilute sulphuric acid. The filtered liquid by gentle evaporation yields alloxanic acid in small radiated needles. It has an acid taste and reaction, decomposes carbonates, and dissolves zinc with disengagement of hydrogen. It is a bibasic acid, represented in the hydrated state by ($C_8H_2N_2O_8,2HO$); hence it is isomeric with alloxan. The alloxanates of the alkalis are freely soluble; those of the earths dissolve in a large quantity of tepid water, and that of silver is quite insoluble and anhydrous.

If a cold, saturated solution of alloxanate of baryta be heated to ebullition, a precipitate falls, which is a mixture of carbonate and alloxanate of baryta with an insoluble salt of a second new acid, the mesoxalic; the solution is found to contain undecomposed alloxanate of baryta and urea. Mesoxalic acid is best prepared by slowly adding solution of alloxan to a boiling-hot solution of acetate of lead; the heavy granular precipitate of mesoxalate of lead thus produced is washed and decomposed by sulphuretted hydrogen; urea is also formed in this experiment. Solution of mesoxalic acid is crystallizable; it has a sour taste and powerfully acid reaction, and resists a boiling heat: it forms sparingly soluble salts with baryta and lime, and a yellowish insoluble compound with oxide of silver, which is reduced with effervescence when gently warmed. The mesoxalic acid contains as hydrate $C_3O_4,2HO$, and is consequently bibasic; it is formed by the resolution of alloxan into urea and 2 eq. of mesoxalic acid:—

$$C_8H_4N_2O_{10} + 2HO = C_2H_4N_2O_2 + 2(HO,C_3O_4).$$

When ammonia in excess is added to a solution of alloxan, the whole heated to ebullition, and afterwards supersaturated with dilute sulphuric acid, a yellow, light precipitate falls, which increases in quantity as the liquid cools. This is mykomelinic acid; it is but feebly soluble in water, easily dissolves in alkalis, and forms a yellow compound with oxide of silver. Mykomelinic acid contains $C_8H_5N_4O_5$; it is produced by the conversion of alloxan and 2 eq. of ammonia into 1 eq. of mykomelinic acid and 5 eq. of water.

Parabanic Acid.—This is the characteristic product of the action of moderately strong nitric acid on uric acid or alloxan, *by the aid of heat*; it is conveniently prepared by heating together 1 part of uric acid and 8 parts of nitric acid until the reaction has nearly ceased; the liquid is evaporated to a syrupy state, and left to cool; the acid is drained from the mother-liquid and purified by re-crystallization. Parabanic acid forms beautiful colourless, transparent, thin, prismatic crystals, which are permanent in the air; it is easily soluble in water, has a pure and powerful acid taste, and reddens litmus strongly. Neutralized with ammonia, and mixed with nitrate of silver, it gives a white precipitate. Crystallized parabanic acid contains $C_6N_2O_4,2HO$; its production is thus explained: 1 eq. of uric acid, 2 eq. of water and 4 eq. of oxygen from the nitric acid, yield 1 eq. of parabanic acid, 4 eq. of carbonic acid, and 2 eq. of ammonia; or, alloxan and four additional equivalents of oxygen furnish 1 eq. of parabanic acid, 2 eq. of carbonic acid, and 4 eq. of water.

The alkaline parabanates undergo a singular change by exposure to heat; if a solution of the acid be saturated with ammonia, boiled for a moment, and then left to cool, a substance separates in tufts of beautiful colourless needles; this is the ammonia-salt of an acid called the *oxaluric*. The hydrated acid is procured by adding an excess of dilute sulphuric acid to a hot and strong solution of oxalurate of ammonia, and cooling the whole rapidly. It forms a white, crystalline powder, of acid taste and reaction, capable of combining with bases: the salts of baryta and lime are sparingly

le; that of *silver* crystallizes from the mixed hot solution of nitrate of e and oxalurate of ammonia in long, silky needles. Oxaluric acid is osed of $C_6H_3N_2O_7,HO$; or the elements of 1 eq. of parabanic acid and of water. A solution of oxaluric acid is resolved by ebullition into oxalic acid and oxalate of urea.

HIONURIC ACID.—A cold solution of alloxan is mixed with a saturated tion of sulphurous acid in water, in such quantity that the odour of the remains quite distinct; an excess of carbonate of ammonia mixed with tle caustic ammonia is then added, and the whole boiled for a few ites. On cooling, *thionurate of ammonia* is deposited in great abundance, ing beautiful colourless, crystalline plates, which by solution in water re-crystallization acquire a fine pink tint. A solution of this salt gives acetate of lead a precipitate of insoluble thionurate of the oxide of metal, which is at first white and gelatinous, but shortly becomes dense crystalline; from this compound the hydrated acid may be obtained by id of sulphuretted hydrogen. It forms a white, crystalline mass, per- ent in the air, very soluble in water, of acid taste and reaction, and ble of combining directly with bases. When its solution is heated to oiling-point, it undergoes decomposition, yielding sulphuric acid and a peculiar and nearly insoluble substance, called *uramile*. Thionuric acid basic; the hydrate contains $C_8H_5N_3S_2O_{12},2HO$; or the elements of an, an equivalent of ammonia, and 2 eq. of sulphurous acid.

AMILE.—The product of the decomposition by heat of hydrated thionu- cid. Thionurate of ammonia is dissolved in hot water, mixed with a excess of hydrochloric acid, and the whole boiled in a flask; a white, alline substance begins in a few moments to separate, which increases antity until the contents of the vessel often become semi-solid; this is ile. After cooling, it is collected on a filter, washed with cold water to ve the sulphuric acid, and dried by gentle heat, during which it fre- tly becomes pinkish. Examined by a lens, it is seen to consist of te acicular crystals. It is tasteless and nearly insoluble in water, but lves in ammonia and the fixed alkalis. The ammoniacal solution be- s purple in the air. It is decomposed by strong nitric acid, alloxan nitrate of ammonia being generated. Uramile contains $C_8H_5N_3O_6$; or uric acid *minus* the elements of 2 eq. of sulphuric acid.

AMILIC ACID.—When a cold saturated solution of thionurate of ammo- s mixed with dilute sulphuric acid, and evaporated in a water-bath, d of uramile, another substance, *uramilic acid*, is formed and deposited nder, colourless prisms, soluble in 8 parts of cold water. Uramilic dissolves in concentrated sulphuric acid without apparent decomposi- it has a feeble acid taste and reaction, and combines with bases. The of the alkalis are easily soluble; those of the earths much less so, and of the oxide of silver is insoluble. Uramilic acid contains $C_{16}H_{10}N_5O_{15}$; of uramile and 3 eq. of water contain the elements of uramilic acid eq. of ammonia. It is a substance difficult of preparation.

LOXANTIN.—This is the chief product of the action of hot *dilute* nitric upon uric acid; the surest and best method of preparing it, however, passing a stream of sulphuretted-hydrogen gas through a moderately g and cold solution of alloxan. The impure mother-liquid from which rystals of alloxan have separated answers the purpose perfectly well diluted with a little water, and a copious stream of gas transmitted igh it. Sulphur is deposited in large quantity, mixed with a white, alline substance, which is the alloxantin. The product is drained upon er, slightly washed, and then boiled in water; the filtered solution sits the alloxantin on cooling. Alloxantin forms small, four-sided, ue *rhombic prisms*, colourless and transparent; it is soluble with diffi- n *cold water, but* more freely at a boiling temperature. The solution

reddens litmus, gives with baryta-water a violet-coloured precipitate, which disappears on heating, and when mixed with nitrate of silver produces a black precipitate of metallic silver. Heated with chlorine or nitric acid, it is changed by oxidation to alloxan. The crystals become red when exposed to ammoniacal vapours. Alloxantin contains $C_8H_5N_2O_{10}$; or alloxan plus 1 equivalent of hydrogen.

This substance is readily decomposed; when a stream of sulphuretted hydrogen is passed through a boiling solution, sulphur is deposited and an acid liquid produced, supposed to contain a new acid, to which the term *dialuric* is applied. When neutralized by ammonia it yields a salt which crystallizes in colourless silky needles, containing $NH_4O,C_8N_2O_4 + 2HO$. They become deep red when heated to 212° (100°C) in the air. A hot saturated solution of alloxantin mixed with a neutral salt of ammonia instantly assumes a purple colour, which however quickly vanishes, and the liquid becomes turbid from the formation of uramile; the liquid is then found to contain alloxan and free acid. With oxide of silver, alloxantin disengages carbonic acid, reduces a portion of the metal, and converts the remainder of the oxide into oxalurate. Boiled with water and binoxide of lead, alloxantin gives urea and carbonate of lead.

MUREXIDE; PURPURATE OF AMMONIA OF DR. PROUT.—There are several different methods of preparing this magnificent compound. It may be made directly from uric acid, by dissolving that substance in dilute nitric acid, evaporating to a certain point, and then adding to the warm, but not boiling liquid, a very slight excess of ammonia. In this experiment alloxantin is first produced, which becomes afterwards partially converted into alloxan; the presence of both is requisite to the production of murexide. This process is, however, very precarious, and often fails altogether. An excellent method is to boil for a few minutes in a flask a mixture of 1 part of dry uramile, 1 part of red oxide of mercury, and 40 parts of water, to which two or three drops of ammonia have been added; the whole assumes in a short space of time an intensely deep purple tint, and when filtered boiling-hot, deposits, on cooling, splendid crystals of murexide, unmixed with any impurity. A third, and perhaps even still better process, is that of Dr. Gregory: 7 parts of alloxan and 4 parts of alloxantin are dissolved in 240 parts of boiling water, and the solution added to about 80 parts of cold, strong solution of carbonate of ammonia; the liquid instantly acquires such a depth of colour as to become opaque, and gives on cooling a large quantity of murexide; the operation succeeds best on a small scale.

Murexide[1] crystallizes in small square prisms, which by reflected light exhibit a splendid green metallic lustre, like that of the wing-cases of the rose-beetle and other insects; by transmitted light they are deep purple-red. It is soluble with difficulty in cold water, much more easily at a boiling temperature, and is insoluble in alcohol and ether. Mineral acids decompose it with separation of *murexan*, and caustic potassa dissolves it, with production of a most magnificent purple colour, which disappears when the solution is boiled. Murexide contains, according to Liebig and Wöhler, $C_{12}H_6N_5O_8$; its production may be thus explained; 2 eq. of uramile and 3 eq. of oxygen from the protoxide of mercury give rise to murexide, 1 eq. of alloxanic acid, and 3 eq. of water.

$$2C_8H_5N_3O_6 + 3O = C_{12}H_6N_5O_8,C_4HNO_4 + 3HO.$$

Or, on the other hand, 1 eq. of alloxan, 2 eq. of alloxantin, and 4 eq. of ammonia, yield 2 eq. of murexide and 14 eq. of water.

$$C_8H_4N_2O_{10} + 2C_8H_5N_2O_{10} + 4NH_3 = 2C_{12}H_6N_5O_8 + 14HO.$$

[1] So called from the Tyrian dye, said to have been prepared from a species of murex, a shell-fish.

MUREXAN; PURPURIC ACID OF DR. PROUT.—Liebig directs this substance to be prepared by dissolving murexide in caustic potassa, heating the liquid until the colour disappears, and then adding an excess of dilute suphuric acid. It separates in colourless or slightly yellowish scales, nearly insoluble in cold water. In ammonia it dissolves, and the solution acquires a purple colour by exposure to the air, the murexide being then produced. Murexan is said to contain $C_6H_4N_2O_5$. This substance, and its relation to murexide, require re-examination.

A series of substances closely related to the derivatives of uric acid, will be noticed under the head of Caffeine (see page 450).

Connected with uric acid by similarity of origin, but not otherwise, are two curious and exceedingly rare substances, called *xanthic oxide* and *cystic oxide*.

Xanthic oxide was discovered by Dr. Marcet; it occurs as an urinary calculus, of pale brown colour, foliated texture, and waxy lustre, and is extracted by boiling the pulverized stone in dilute caustic potassa and precipitating by carbonic acid. The xanthic oxide falls as a white precipitate, which on drying becomes pale yellow, and resembles wax when rubbed. It is nearly insoluble in water and dilute acids. Its characteristic property is to dissolve without evolution of gas in nitric acid, and to give on evaporation a deep yellow residue, which becomes yellowish-red on the addition of ammonia or solution of potassa. Xanthic oxide gives on analysis $C_5H_2N_2O_2$.

Cystic oxide.—Cystic oxide calculi, although very rare, are more frequently met with than those of the preceding substance; they have a pale colour, a concentric structure, and often a waxy external crust. The powdered calculus dissolves in great part without effervescence in dilute acids and alkalis, including ammonia; the ammoniacal solution deposits, by spontaneous evaporation, small, but beautiful colourless crystals, which have the form of six-sided prisms and square tables. It forms a saline compound with hydrochloric acid. Caustic alkalis disengage ammonia from this substance by continued ebullition. Cystic oxide contains sulphur; it is composed of $C_6H_6NS_2O_4$.

Uric acid is perfectly well characterized, even when in very small quantity, by its behaviour with nitric acid. A small portion heated with a drop or two of nitric acid in a small porcelain capsule dissolves with copious effervescence. When this solution is cautiously evaporated nearly to dryness, and, after the addition of a little water, mixed with a slight excess of ammonia, the deep red tint of murexide is immediately produced.

Impure uric acid, in a remarkable state of decomposition, is now imported into this country in large quantities, for use as a manure, under the name *guano* or *huano*. It comes from the barren and uninhabited islets of the western coast of South America, and is the production of the countless birds that dwell undisturbed in those regions. The people of Peru have used it for ages. Guano usually appears as a pale brown powder, sometimes with whitish specks; it has an extremely offensive odour, the strength of which, however, varies very much. It is soluble in great part in water, and the solution is found to be extremely rich in oxalate of ammonia, the acid having been generated by a process of oxidation. Guano also contains a peculiar substance called *guanine*, which closely corresponds with xanthic oxide. Like this, it combines with acids, forming a series of crystallizable salts. Guanine contains $C_{10}H_5N_5O_2$.

SECTION V.

THE VEGETO-ALKALIS.

The vegeto-alkalis, or *alkaloids*, or *organic bases*, constitute a remarkable and most interesting group of bodies; they are met with in various plants, always in combination with an acid, which is in many cases of peculiar nature, not occurring elsewhere in the vegetable kingdom. They are, for the most part, sparingly soluble in water, but dissolve in hot alcohol, from which they often crystallise in a very beautiful manner on cooling. Several of them, however, are oily, volatile liquids. The taste of these substances, when in solution, is usually intensely bitter, and their action upon the animal economy exceedingly energetic. They all contain a considerable quantity of nitrogen, and are very complicated in constitution, having high combining numbers. It is probable that these bodies are very numerous.

None of the organic bases occurring in plants have yet been formed by artificial means; analogous substances have, however, been thus produced.

Morphine, or morphia. — This is the chief active principle of opium; it is the best and most characteristic type of the group, and the earliest known, dating back to the year 1803.

Opium, the inspissated juice of the poppy-capsule, is a very complicated substance, containing, besides morphihe, a host of other alkaloids in very variable quantities, combined with sulphuric acid and an organic acid called the *meconic*. In addition to these, there are gummy, resinous, and colouring matters, caoutchouc, &c., besides mechanical impurities, as chopped leaves. The opium of Turkey is the most valuable, and contains the largest quantity of morphine; that of Egypt and of India are considerably inferior. It has been produced in England of the finest quality, but at great cost.

If ammonia be added to a clear, aqueous infusion of opium, a very abundant buff-coloured or brownish-white precipitate falls, which consists principally of morphine and narcotine, rendered insoluble by the withdrawal of the acid. The product is too impure, however, for use. The chief difficulty in the preparation of these substances is to get rid of the colouring matter, which adheres with great obstinacy, re-dissolving with the precipitates, and being again in part thrown down when the solutions are saturated with an alkali. The following method, which succeeds well upon a small scale, will serve to give the student some idea of a process very commonly pursued when it is desired to isolate at once an insoluble organic base, and the acid with which it is in combination:—A filtered solution of opium in tepid water is mixed with acetate of lead in excess: the precipitated meconate of lead is separated by a filter, and through the solution containing acetate of morphine, now freed to a considerable extent from colour, a stream of sulphuretted hydrogen is passed. The filtered and nearly colourless liquid, from which the lead has been thus removed, may be warmed to expel the excess of gas, once more filtered, and then mixed with a slight excess of caustic ammonia, which throws down the morphine and narcotine; these may be separated by boiling ether, in which the latter is soluble. The meconate of lead, well washed,

... by sulphuretted hydrogen, yields solu-

... prepared, on the large scale, by
... usion of opium is mixed with a
... iron; meconate of lime, which is
... drochloric acid is transferred to the
... altered solution, the hydrochlorate of
... while the narcotine, and other bodies,
... lization, and the use of animal charcoal,
... ae salt, from which the base may be pre-
... onia. Other processes have been proposed,
... n consists in adding hydrate of lime in excess
... which the meconic acid is rendered insoluble,
... up with ease by the alkaline earth. By *exactly*
... ution with hydrochloric acid, the morphine is pre-
... hat coloured state.
... tallized from alcohol, forms small, but very brilliant
... ch are transparent and colourless. It requires at least
... for solution, tastes slightly bitter, and has an alkaline
... fects are much more evident in the alcoholic solution. It
... 30 parts of boiling alcohol, and with great facility in dilute
... dissolved by excess of caustic potassa or soda, but scarcely
... mmonia. When heated in the air, morphine melts, inflames
... nd leaves a small quantity of charcoal, which easily burns away.
... , in powder, strikes a deep bluish colour with neutral salts of
... e of iron, decomposes iodic acid with liberation of iodine, and forms
... llow or red compound with nitric acid; these reactions are by some
... red characteristic.

...stalline morphine contains $C_{34}H_{19}NO_6+2HO$.

...e most characteristic and best-defined salt of this substance is the *...ochlorate*. It crystallizes in slender, colourless needles, arranged in tufts ...stallated groups, soluble in about 20 parts of cold water, and in its own ...ght at a boiling temperature. The crystals contain 6 eq. of water. The *...hate*, *nitrate*, and *phosphate* are crystallizable salts; the *acetate* crystallizes ...h great difficulty, and is usually in the state of a dry powder. The arti...al *meconate* is sometimes prepared for medicinal use.

NARCOTINE.—The *marc*, or insoluble portion of opium, contains much nar...tine, which may be extracted by boiling with dilute acetic acid. From the ...tered solution the narcotine is precipitated by ammonia, and afterwards ...rified by solution in boiling alcohol, and filtration through animal charcoal. ...rcotine crystallizes in small, colourless, brilliant prisms, which are nearly ...soluble in water. The basic powers of narcotine are very feeble; it is des...tute of alkaline reaction, and, although freely soluble in acids, refuses, for the most part, to form with them crystallizable compounds.

According to Dr. Blyth, narcotine contains $C_{46}H_{25}NO_{14}$.

Narcotine yields some curious products by the action of oxidizing agents, as a mixture of dilute sulphuric acid and binoxide of manganese, or a hot solution of bichloride of platinum. They have been chiefly studied by Wöhler and Blyth, and lately also by Anderson. The most important of these is *opianic acid*, a substance forming colourless, prismatic, reticulated crystals, sparingly soluble in cold water, easily in hot. It melts when heated, but does not sublime. After fusion it becomes quite insoluble in dilute alkalis, but without change of composition. This acid forms crystallizable salts and an ether: it contains $C_{20}H_9O_9HO$. The ammonia-salt, by evaporation to dryness, yields a nearly white insoluble powder, called *opiammon*, containing $C_{40}H_{19}NO_{10}$, convertible by strong acids into opianic acid and ammonia. Sol-
[illegible]

phurous acid yields with opianic acid two products containing sulphur. A mixture of binoxide of lead, opianic acid, and sulphuric acid gives rise to a crystallizable bibasic acid termed *hemipinic acid*, containing $C_{20}H_8O_{10}.2HO$. A basic substance, *cotarnine*, $C_{26}H_{13}NO_6$, is contained in the mother-liquor from which opianic acid has crystallized; it forms a yellow crystalline mass, very soluble, of bitter taste, and feebly alkaline reaction. Its hydrochlorate is a well-defined salt. Another basic substance, *narcogenine*, was accidentally produced in an attempt to prepare cotarnine by bichloride of platinum. It formed large orange-coloured needles, and contained $C_{36}H_{19}NO_{10}$.

CODEINE. — Hydrochlorate of morphine, prepared directly from opium as in Gregory's process, contains codeine-salt. When dissolved in water, and mixed with a slight excess of ammonia, the morphine is precipitated, and the codeine left in solution. Pure codeine crystallizes, by spontaneous evaporation, in colourless transparent octahedrons; it is soluble in 80 parts of cold, and 17 of boiling water, has a strong alkaline reaction, and forms crystallizable salts.

Codeine is composed of $C_{36}H_{21}NO_6$. This has lately been the subject of a careful investigation by Dr. Anderson, who has prepared a great number of its derivatives, all of which establish the formula given.

THEBAINE OR PARAMORPHINE.—This substance is contained in the precipitate formed by hydrate of lime in a strong infusion of opium in Thiboumery's process for morphine. The precipitate is well washed, dissolved in dilute acid, and mixed with ammonia in excess, and the thebaine thrown down, crystallized from alcohol. It forms when pure colourless needles like those of narcotine, but sparingly soluble in water, readily soluble in the cold in alcohol and ether. It melts when heated, and decomposes at a high temperature. With dilute acids it forms crystallizable compounds, and when isolated and in solution has a powerful alkaline reaction. The composition of thebaine is $C_{38}H_{21}NO_6$.

A series of other bases, *pseudo-morphine*, *narceine*, *meconine*, *papaverine*, *opianine*, and *porphyroxine*, are also, at least occasionally, contained in opium; they are of small importance, and comparatively little is known respecting them.

MECONIC ACID is obtained from the impure meconate of lead, as already mentioned. The solution is evaporated in the vacuum of the air-pump. A more advantageous method is to decompose the impure meconate of lime, obtained in Dr. Gregory's morphine-process, by warm dilute hydrochloric acid; to separate the crystals of acid meconate of lime, which form on cooling, and to repeat this operation until the whole of the base has been removed, which may be known by the acid being entirely combustible, without residue, when heated in the flame of a spirit-lamp upon platinum foil. It is with the greatest difficulty obtained free from colour.

Meconic acid crystallizes in little colourless, pearly scales, which dissolve in 4 parts of hot water. It has an acid taste and reaction, forms soluble compounds with the alkalis, and insoluble salts with lime, baryta, and the oxides of lead and silver. The most remarkable feature in this substance is its property of striking a deep blood-red colour with a salt of the sesquioxide of iron, exactly resembling that developed, under similar circumstances, by a sulphocyanide. The meconate of iron may, however, be distinguished from the latter compound, as Mr. Everitt has shown, by an addition of corrosive sublimate, which bleaches the sulphocyanide, but has little effect upon the meconate. This is a point of considerable practical importance, as in medico-legal inquiries, in which evidence of the presence of opium is sought for in complex organic mixtures, the detection of meconic acid is usually the object of the chemist; and since traces of alkaline sul-

hocyanide are to be found in the saliva, it becomes very desirable to remove iat source of error and ambiguity.

Crystallized meconic acid contains $C_{14}HO_{11},3HO+6HO$.

When a solution of meconic acid in water, or, still better, in a mineral cid, is boiled, or when the dry acid is exposed in a retort to a temperature f 400° (204°·5C), it is decomposed, yielding a new *bibasic* acid, the *comenic*, ontaining $C_{12}H_2O_8,2HO$, which much resembles in properties meconic acid. Water and carbonic acid are at the same time extricated. At a higher temperature comenic acid itself is resolved into a second new acid, the *pyromeconic*, which sublimes, and afterwards condenses in brilliant colourless plates. It is monobasic, and contains $C_{10}H_3O_5,HO$. The salts of meconic acid and comenic acid, together with several derivatives of these substances, have been lately studied by Mr. How,[1] but our space will not permit us to describe these compounds.

An acid much resembling the meconic has been extracted from the *Chelidonium majus;* it is combined with lime, and associated with malic and fumaric acids. Chelidonic acid is bibasic, forming three classes of salts, and a pyro-acid with evolution of water and carbonic acid when exposed to a high temperature. It crystallizes in slender colourless needles of considerable solubility, containing $C_{14}H_2O_{10},2HO+3HO$.

CINCHONINE AND QUININE.—It is to these vegeto-alkalis that the valuable medicinal properties of the Peruvian barks are due. They are associated in the bark with sulphuric acid, and with a special acid, not found elsewhere, called the *kinic.* Cinchonine is contained in largest quantity in the pale bark, or *Cinchona condaminea;* quinine in the yellow bark, or *Cinchona cordifolia;* the *Cinchona oblongifolia* contains both.

The simplest, but not the most economical, method of preparing these substances, is to add a slight excess of hydrate of lime to a strong decoction of the ground bark, in acidulated water; to wash the precipitate which ensues, and boil it in alcohol. The solution, filtered while hot, deposits the vegeto-alkali on cooling. When both bases are present, they may be separated by converting them into sulphates; the salt of quinine is the least soluble of the two, and crystallizes first.

Pure cinchonine or cinchonia, crystallizes in small, but beautifully brilliant, transparent four-sided prisms. It is but very feebly soluble in water, dissolves readily in boiling alcohol, and has but little taste, although ts salts are excessively bitter. It is a powerful base, neutralizing acids ompletely, and forming a series of crystallizable salts.

Quinine, or quina, much resembles cinchonine; it does not crystallize so 'ell, however, and is much more soluble in water; its taste is intensely itter.

Cinchonine is composed of .... $C_{20}H_{12}NO$, and
Quinine of .... $C_{20}H_{12}NO_2$.[2]

Sulphate of quinine is manufactured on a very large scale for medicinal se; it crystallizes in small white needles, which give a neutral solution. evertheless, this substance is a basic salt, and contains $2C_{20}H_{12}NO_2,SO_3+$ HO. The solubility of this compound is much increased by the addition of little sulphuric acid, whereby the neutral salt $C_{20}H_{12}NO_2,SO_3+8HO$ is ormed. A very interesting compound has been lately produced by Dr.

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[1] Chem. Sec. Quar. Jour. Vol. IV. page 363.

[2] Some doubts are still hanging over the composition of cinchonine and quinine. Accordg to M. Lavrent these substances contain respectively $C_{38}H_{24}N_2O_4$, and $C_{38}H_{24}N_2O_2$. If these rmulæ be adopted the basic sulphate of commerce would become a neutral, the neutral a acid-salt.

Commercial sulphate .... $C_{38}H_{24}N_2O_2SO_3+8HO$
Soluble sulphate .... $C_{38}H_{24}N_2O_2,SO_3+HO,SO_3+15HO$.

Herapath, by the action of iodine upon the sulphate of quinine. It is a crystalline substance of a brilliant emerald colour, which appears to consist of 1 eq. of the sulphate of quinine, and 1 eq. of iodine. This remarkable compound possesses the optical properties of the mineral tourmaline. (See page 75.)

Quinidine.—In manufacturing sulphate of quinine, a new base has been lately obtained, which differs from quinine in some of its physical properties, but is said to have the same composition as quinine. It has been described under the name of quinidine, and appears to have the same medicinal properties as quinine. This substance is not yet sufficiently examined.[1]

Chinoidine, quinoidine, or amorphous quinine, is contained in the refuse mother-liquors of the quinine-manufacture. In its present state it forms a yellow or brown resin-like mass, insoluble in water, freely soluble in alcohol and ether. It is easily soluble also in dilute acids, and is thence precipitated by ammonia. Quinoidine possesses powerful febrifuge properties, and is identical in composition with quinine. It evidently bears to quinine the same relation that uncrystallizable syrup does to ordinary sugar, being produced from quinine by the heat employed in the preparation.[2]

From *Cusco*, or *Arica-bark*, and likewise from the *Cinchona ovata*, or *quinquina* of Condamine, a substance denominated *aricine* or *cinchovatine* has been extracted; it closely resembles cinchonine, and contains $C_{20}H_{12}NO_3$, 1 eq. of oxygen more than quinine, and 2 eq. more than cinchonine.

This substance is useless in medicine.

Kinic acid.—Kinate of lime is found in the solution from which the vegeto-alkalis have been separated by hydrate of lime, and is easily obtained by evaporation, and purified by animal charcoal. From the lime-salt the acid can be extracted by decomposing it by diluted sulphuric acid. The clear solution evaporated to a syrupy consistence deposits large, distinct crystals, which resemble those of tartaric acid. It is soluble in 2 parts of water, and contains $C_{14}H_{11}O_{11}.HO$.

When kinic acid is heated with a mixture of sulphuric acid and binoxide of manganese, it furnishes a very volatile substance termed *kinone*, the vapour of which is exceedingly irritating to the eyes. This new body forms crystals both by sublimation and by solution in boiling water; it melts with gentle heat, and crystallizes on cooling, colours the skin permanently brown, and contains $C_{12}H_4O_4$.

By destructive distillation, kinic acid yields numerous and interesting products, which have been studied by M. Wöhler, as benzoic acid, carbolic acid, hydride of salicyl, benzol, a tarry substance not examined, and a new body, *colourless hydrokinone*, which possesses very curious relations with the kinone above described. It forms colourless six-sided prismatic crystals; is neutral, destitute of taste and odour, fusible, and easily soluble both in water

[1] Quina is very soluble in alcohol and ether; its sulphate requires 57 parts of absolute and 63 of alcohol of 90 per cent. for solution; of water 265 parts of cold and 24 of boiling are required. The oxalate is completely insoluble in water.

Quinidine differs in separating from its solution in alcohol in crystals, in its inferior solubility in alcohol and ether, and the greater solubility of its sulphate in water. It dissolves in 140 to 150 parts of ether, 45 of absolute and 105 of alcohol of 90 per cent. Its sulphate is soluble in 32 parts of absolute and 7 parts of alcohol of 90 per cent., in 73 parts of cold and less than 5 of boiling water, according to Howard (130 of 62°·6 (17°C) and 16 of boiling water.—Leers). The oxalate is very soluble in cold and more freely in boiling water, from which crystals are deposited on cooling.

Quinidine contains $C_{18}H_{11}NO$.—R. B.

[2] Amorphous quinine is a mixture of quina, cinchonia, and a resin. Quina may be obtained from it by dissolving in alcohol, precipitating by protochloride of tin, filtering, and adding ammonia to the clear liquor. The precipitate well washed and dried, and a second time treated with protochloride of tin and ammonia, yields to alcohol pure quina, which crystallizes on evaporating the alcohol.—R. B.

alcohol. With care it may be sublimed unchanged. It contains [illegible]$_6O_4$.

[illegible]olourless hydrokinone can be easily and directly produced from kinone [illegible]he assimilation of hydrogen, as by addition of hydriodic acid to a solu[illegible] of the latter, when iodine is set free, or by sulphurous acid, or tellu[illegible]ed hydrogen.

[illegible]n intermediate product of reduction is *green hydrokinone*. This is ob[illegible]ed by the incomplete action of sulphurous acid upon kinone, or by the [illegible]on of sesquichloride of iron, chlorine, nitrate of silver, or chromic acid [illegible]n colourless hydrokinone; or by mixing together solutions of kinone and [illegible]urless hydrokinone. It forms slender green crystals of the colour of the [illegible]g-case of the rose-beetle, and of the greatest brilliancy and beauty. It [illegible]sible, has but little odour, and dissolves freely in boiling water, crys[illegible]izing out on cooling. This substance contains $C_{12}H_5O_4$.

[illegible]f kinic acid be submitted to distillation with an ordinary chlorine-mix[illegible]e, an acid liquid and a crystalline sublimate are formed. The former is [illegible]olution of formic acid, the latter a mixture of 4 chlorinetted compounds, [illegible]ch are chlorokinone $C_{12}(H_3Cl)O_4$, bichlorokinone $C_{12}(H_2Cl_2)O_4$, trichloro[illegible]one $C_{12}(HCl_3)O_4$ and tetrachlorokinone $C_{12}Cl_4O_4$. They are all yellow [illegible]stalline substances, which can be separated only with great difficulty. [illegible]e kinone itself, they possess the faculty of combining with 1 or 2 eq. of [illegible]drogen, producing 2 series of substances analogous to green and colour[illegible] hydrokinone. Tetrachlorokinone, better known by the name *chloranile*, [illegible]wise occurs among the products of decomposition of indigo.

[illegible]ther products were obtained by the action of sulphuretted hydrogen and [illegible]ng hydrochloric acid upon kinone, which possess less interest than the [illegible]eding.

[illegible]TRYCHNINE AND BRUCINE, also called strychnia and brucia, are contained [illegible] *Nux vomica*, in *St. Ignatius' bean*, and in *false Angustura bark;* they are [illegible]ciated with a peculiar acid, called the *igasuric*. Nux vomica seeds are [illegible]ed in dilute sulphuric acid until they become soft; they are then [illegible]hed, and the expressed liquid mixed with excess of hydrate of lime, [illegible]ch throws down the alkalis. The precipitate is boiled in spirit of wine [illegible]p. gr. 0·850, and filtered hot. Strychnine and brucine are deposited [illegible]ther in a coloured and impure state, and may be separated by cold [illegible]hol, in which the latter dissolves readily.

[illegible]ure strychnine crystallizes under favourable circumstances in small, but [illegible]eedingly brilliant octahedral crystals, which are transparent and colour[illegible]. It has a very bitter, somewhat metallic taste (1 part in 1,000,000 parts [illegible]water is still perceptible), is slightly soluble in water, and is fearfully [illegible]onous. It dissolves in hot, and somewhat dilute spirit, but neither in [illegible]olute alcohol, ether, nor in solution of caustic alkali. This alkaloid may [illegible]readily identified by moistening a crystal with concentrated sulphuric [illegible], and adding to the liquid a crystal of bichromate of potassa, when a [illegible] violet tint is produced, which disappears after some time. Strychnine [illegible]s with acids a series of well-defined salts, lately examined by Messrs. [illegible]holson and Abel, who established for strychnine the formula $C_{42}H_{22}N_2O_4$

[illegible]rucine is easily distinguished from the preceding substance, which it [illegible]h resembles in many respects, by its ready solubility in alcohol, both [illegible]rate and absolute. It dissolves also in about 500 parts of hot water. [illegible] salts of brucine are, for the most part, crystallizable.

[illegible]rucine contains $C_{46}H_{26}N_2O_8$.

[illegible]ERATRINE (or veratria) is obtained from the seeds of *Veratrum sabadilla*. [illegible]ts purest state it is a white, or yellowish-white powder, which has a sharp [illegible]ning taste, and is very poisonous. It is remarkable for occasioning violent [illegible]zing. It is insoluble in water, but dissolves in hot alcohol, in ether, and

in acids; the solution has an alkaline reaction. Veratrine contains nitrogen, but its composition is yet doubtful.[1]

A substance called *colchicine*, extracted from the *Colchicum autumnale*, and formerly confounded with veratrine, is now considered distinct; its history is yet imperfect.

CONINE (CONICINE, OR CONIA), NICOTINE, and SPARTEINE, differ from the other vegetable bases in physical characters; they are volatile oily liquids. The first is extracted from hemlock, the second from tobacco, and the third from broom (*spartium scoparium*). They agree in most of their characters, having high boiling-points, very poisonous properties, strong alkaline reaction, and the power of forming with acids crystallizable salts. The formula of nicotine is $C_{10}H_7N$; that of conine, $C_{16}H_{15}N$, and that of sparteine $C_{15}H_{13}N$. A series of substances as it appears closely related to nicotine will be mentioned among the artificial organic bases.

The basic substance contained in the juice of animal flesh, *kreatinine*, will be found described among the components of the animal body.

HARMALINE. — This compound is extracted by dilute acetic acid from the seeds of the *Peganum harmala*, a plant which grows abundantly in the Steppes of Southern Russia, and the seeds of which are used in dyeing. When pure, it forms yellowish prismatic crystals, soluble in alcohol and dilute acids, but scarcely forming crystallizable salts. By oxidation it gives rise to another compound, *harmine*, which itself possesses basic properties. The seeds are used for dyeing. Harmaline probably contains $C_{26}H_{14}N_2O_2$, and harmine $C_{26}H_{12}N_2O_2$.

CAFFEINE, OR THEINE. — This remarkable substance occurs in four articles of domestic life, infusions of which are used as a beverage over the greater part of the known world, namely, tea and coffee, and the leaves of *Guarana officinalis*, or *Paullinia sorbilis*, and in those of *Ilex paraguayensis;* it will probably be found in other plants. A decoction of common tea, or of raw coffee-berries, previously crushed, is mixed with excess of solution of basic acetate of lead. The solution, filtered from the copious yellow or greenish precipitate, is treated with sulphuretted hydrogen to remove the lead, filtered, evaporated to a small bulk, and neutralized by ammonia. The caffeine crystallizes out on cooling, and is easily purified by animal charcoal. It forms tufts of delicate, white, silky needles, which have a bitter taste, melt when heated with loss of water, and sublime without decomposition. It is soluble in about 100 parts of cold water, and much more easily at a boiling-heat, or if an acid be present. Alcohol also dissolves it, but not easily. Caffeine contains $C_{16}H_{10}N_2O_4$. The basic properties are feeble. The salts with hydrochloric and sulphuric acid are obtained only with difficulty. It forms, however, splendid double-salts with bichloride of platinum and terchloride of gold. The products of oxidation of caffeine, which have been lately studied by Rochleder, are of considerable interest, inasmuch as both their composition and their properties establish a close connection of these products with the derivatives of uric acid. Under the influence of chlorine, caffeine yields a substance of feebly acid properties, which contains $C_{12}H_7N_2O_8$. This compound, which has received the name *amalic acid*, is homologous to alloxantin. When treated with oxidizing agents, it yields *cholestrophane*, $C_{10}H_6N_2O_6$, the parabanic acid of the uric acid-series. The murexide of the caffeine-series lastly is formed by the treatment of amalic acid with ammonia.

[1] According to Courbe, it contains $C_{34}H_{22}NO_6$. Several of these bases may be distinguished by nitric acid. Brucia becomes bright red, which is soon changed to purple by chloride of tin. Pure strychnine becomes yellow. Veratria, orange red, soon changing to yellow. Morphia, bright red, changed to yellow by chloride of tin.—R. B.

actly as the murexide *par excellence* is formed by the action of ammonia on alloxantin. The new murexide imitates its prototype not only in composition, but likewise in the green metallic lustre of its crystals, and the deep crimson colour of its solutions. The homology of these compounds with the members of the uric acid-series is well illustrated by a comparison of their formulæ —

Alloxantin	$C_8H_8N_2O_8 + 2C_2H_2 = C_{12}H_7N_2O_8$	Amalic acid
Parabanic acid	$C_6H_2N_2O_6 + 2C_2H_2 = C_{10}H_6N_2O_6$	Cholestrophane
Murexide	$C_{12}H_6N_5O_8 + 3C_2H_2 = C_{18}H_{12}N_5O_8$	Caffeine-murexide

THEOBROMINE. — The seeds of the *Theobroma cacao*, or cacao-nuts, from which chocolate is prepared, contain a crystallizable principle to which the preceding name is given. It is extracted in the same manner as caffeine, and forms a white, crystalline powder, which is much less soluble than the last-named substance. It contains, according to Glasson, $C_{14}H_8N_4O_4$. Accordingly it is homologous to caffeine. The products obtained from theobromine by oxidation appear to be likewise homologous with terms of the uric acid-series.

BERBERINE.—A substance crystallizing in fine yellow needles, slightly soluble in water, extracted from the root of the *Berberis vulgaris*. It has feeble basic properties, and contains $C_{42}H_{18}NO_9$. This must not be confounded with *beeberine*, an uncrystallizable basic substance, from the bark of the *green-heart* timber of Guiana, which has the composition $C_{38}H_{21}NO_6$. It forms with acids uncrystallizable salts.

PIPERINE.—A colourless, or slightly yellow crystallizable principle, extracted from pepper by the aid of alcohol. It is insoluble in water. Formula $C_{34}H_{19}NO_6$. Piperine readily dissolves in acid; definite compounds however are obtained only with difficulty.

There are very many other bodies, more or less perfectly known, having to a certain extent the properties of salt-bases; the following statement of the names and mode of occurrence of a few of these must suffice.

Hyoscyamine (*Daturine*).—A white, crystallizable substance, from *Hyoscyamus niger;* it occurs likewise in *Datura stramonium*, formula $C_{34}H_{23}NO_6$.

Atropine.—Colourless needles, from *Atropa belladonna*, formula $C_{34}H_{23}NO_6$.[1]

Solanine.—A pearly, crystalline substance, from various solanaceous plants.

Aconitine.—A glassy, transparent mass, from *Aconitum napellus:* formula $C_{60}H_{47}NO_{14}$.[2]

Delphinine.—A yellowish, fusible substance, from the seeds of *Delphinium staphisagria.*

Emetine.—A white and nearly tasteless powder from ipecacuanha root.

Curarine.—The arrow-poison of Central America.

There exists an extensive series of neutral, usually bitter, and sometimes poisonous vegetable principles, which are allied in some measure to the vegeto-alkalis. Some of these are destitute of nitrogen. Two of the number, salicin and phloridzan, have been already described (see pages 403 and 406); the most important of the remainder are the following:—

GENTIANIN.—The bitter principle of the gentian-root, extracted by ether.

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[1] Crystallizes from a saturated hot aqueous solution in silky tufts; colourless, inodorous, very bitter, soluble in 25 parts of ether, 2000 parts cold and 54 of hot water. Has a strong alkaline reaction, and forms crystallizable salts. It is probably identical with daturine.—R. B.

[2] Crystallizes from an alcoholic solution in small grains; soluble readily in alcohol and ether, and also in 160 parts cold and 50 boiling water; has a sharp, bitter taste, and alkaline reaction. Its salts are not crystallizable.—R. B.

It crystallizes in golden-yellow needles, is sparingly soluble in cold water, more soluble in hot water, and freely dissolved by alcohol and ether. Its composition is $C_{14}H_6O_5$.

POPULIN.—This substance closely resembles salicin in appearance and solubility, but has a penetrating sweet taste; it is found accompanying salicin in the bark and leaves of the aspen. According to recent researches of Piria, populin contains $C_{40}H_{22}O_{16}+4HO$. It is a conjugate compound of salicin and benzoic acid.

$$\underbrace{C_{40}H_{22}O_{16}}_{\text{Crystall. Populin.}} = \underbrace{C_{14}H_6O_4}_{\text{Benzoic acid.}} + \underbrace{C_{26}H_{18}O_{14}}_{\text{Salicin.}} + 2HO$$

By the action of reagents it is converted into benzoic acid, and the products of decomposition of salicin. With dilute acid it yields benzoic acid, grape-sugar, and saliretin; when treated with a mixture of sulphuric acid and bichromate of potassa, it furnishes a considerable quantity of hydride of salicyl.

DAPHNIN.—Extracted from the bark of the *Daphne mezereum*; it forms colourless, radiated needles, freely soluble in hot water, alcohol and ether.

HESPERIDIN.—A white, silky, tasteless substance, obtained from the spongy part of oranges and lemons. It dissolves in 60 parts of hot water; also in alcohol and ether.

ELATERIN.—The active principle of *Momordica elaterium*. It is a white, silky, crystalline powder, insoluble in water. It has a bitter taste, and excessively violent purgative properties. Alcohol, ether, and oils dissolve it. Exposed to heat, it melts and afterwards volatilizes. It contains $C_{20}H_{14}O_5$.

ANTIARIN.—The poisonous principle of the *Upas antiar*. It forms small pearly crystals, soluble in 27 parts of boiling water, and also in alcohol, but scarcely so in ether; it cannot be sublimed without decomposition. Introduced into a wound, it rapidly brings on vomiting, convulsions, and death. Antiarin contains $C_{14}H_{10}O_5$.

PICROTOXIN.—It is to this substance that *Cocculus indicus* owes its active properties. Picrotoxin forms small, colourless, stellated needles, of inexpressibly bitter taste, which dissolve in 25 parts of boiling alcohol. It contains $C_{10}H_6O_4$.

ASPARAGIN.—This, and the two following, are azotized bodies. Asparagin is found in the root of the marsh-mallow, in asparagus sprouts, and in several other plants. The mallow-roots are chopped small, and macerated in the cold with milk of lime: the filtered liquid is precipitated by carbonate of ammonia, and the clear solution evaporated in a water-bath to a syrupy state. The impure asparagin, which separates after a few days, is purified by re-crystallization. Asparagin forms brilliant, transparent, colourless crystals, which have a faint cooling taste, and are freely soluble in water, especially when hot. When dissolved in a saccharine liquid, which is afterwards made to ferment, when heated with water under pressure in a close vessel, or when boiled with an acid or an alkali, it is converted into ammonia and a new acid, the *aspartic*. Asparagin contains $C_8H_8N_2O_6$, and aspartic acid $C_8H_7NO_8$. The remarkable relation in which these substances stand to malic acid has been already noticed under the head of malic acid (see p. 415).

SANTONIN.—This substance is the crystalline principle of several varieties of *Artemisia*. In order to obtain it, the seeds are crushed, and digested with lime and spirit of wine, when a yellow liquid is obtained, from which the alcohol is separated by distillation. The residuary liquid is saturated with acetic acid, when the santonin crystallizes. This substance is easily soluble in water and alcohol, and contains $C_{30}H_{18}O_6$. Santonin possesses the character of a weak acid.

ORGANIC BASES OF ARTIFICIAL ORIGIN.

The constitution of the alkaloids, which occur ready formed in nature, not yet clearly understood. The fact that all these substances contain trogen,—the alkaline reaction, which the greater part of them exhibits th vegetable colours, and especially their faculty of combining with acids crystallizable salts, establish an obvious relation between the alkaloids id ammonia. This has never been doubted, and the views of chemists ive been divided only as to the form of this relation. At a certain time erzelius assumed that all the alkaloids contained ammonia ready formed, id that their basic properties were due to this ammonia. According to is view the formulæ of quinine and morphine would be—

$$\text{Quinine} \ldots\ldots\ldots\ldots \quad C_{20}H_{12}NO_2 = C_{20}H_9\,O_2,NH_3$$
$$\text{Morphine} \ldots\ldots\ldots\ldots \quad C_{34}H_{19}NO_6 = C_{34}H_{16}O_6,NH_3.$$

iis view, in the general form in which it was proposed, is certainly inadissible. It is supported by very scanty experimental evidence, and was ver universally adopted. There may be some alkaloids so constituted as presented by the theory of Berzelius. There are, however, a great many, e constitution of which is obviously different. Several of these substances ive been lately the subject of extensive and careful inquiries; but these searches, although they have established their formulæ and increased our iowledge regarding their salts, have as yet elicited but few facts which omise to afford a clearer insight into the nature of these bodies.

On the other hand, the labours of the last ten years have brought to light very numerous group of substances perfectly analogous to the alkaloids hich are found in plants, but produced by artificial processes in the laboitory. These bodies, which are termed *artificial alkaloids* or *artificial oric bases*, are mostly volatile. Their constitution is much simpler than iat of the native bases. The very processes which give rise to their formaon often permit a very clear insight into the mode in which the elements re grouped, and in the relation existing between these substances and amionia.

In a former section of this volume (page 232), it has been stated that the iajority of chemists incline to assume in the ammoniacal salts the existence f a compound metal ammonium NH_4,

$$\text{Chloride of ammonium, } NH_4Cl$$
$$\text{Sulphate of ammonia, } NH_4O,SO_3.$$

'ow, recent researches have shown, that in these salts, 1, 2, 3, or even the eq. of hydrogen may be replaced by compound radicals, containing varible proportions of carbon and hydrogen, without any change in their funamental properties. It is evident that we obtain in this manner, in addiion to the ammoniacal salts, four new series of compounds very closely llied to the former. Let A B C D represent a series of such radicals capable f replacing hydrogen, then the following series of salts may be 'ormed:—

$$\textbf{Ammonia-salts} \ldots\ldots\ldots \quad N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right\}Cl \ldots\ldots\ldots \quad N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right\}O,SO_3.$$

$$\textbf{First group of compound ammonia-salts} \ldots\ldots \quad N\left\{\begin{matrix}A\\H\\H\\H\end{matrix}\right\}Cl \ldots\ldots\ldots \quad N\left\{\begin{matrix}A\\H\\H\\H\end{matrix}\right\}O,SO_3.$$

Second group of compound ammonia-salts $N\left\{\begin{matrix}A\\B\\H\\H\end{matrix}\right\}Cl$ .... $N\left\{\begin{matrix}A\\B\\H\\H\end{matrix}\right\}O,SO_3$

Third group of compound ammonia-salts .... $N\left\{\begin{matrix}A\\B\\C\\H\end{matrix}\right\}Cl$ .... $N\left\{\begin{matrix}A\\B\\C\\H\end{matrix}\right\}O,SO_3$

Fourth group of compound ammonia-salts $N\left\{\begin{matrix}A\\B\\C\\D\end{matrix}\right\}Cl$ .... $N\left\{\begin{matrix}A\\B\\C\\D\end{matrix}\right\}O,SO_3$

It need scarcely be mentioned that it is by no means necessary that the several hydrogen-equivalents in ammonia should be replaced by different radicals, as assumed in the preceding table. Substances of the formulæ—

$$N\left\{\begin{matrix}A\\A\\H\\H\end{matrix}\right\}Cl \;\ldots\ldots\ldots\; N\left\{\begin{matrix}A\\A\\A\\H\end{matrix}\right\}Cl \;\ldots\ldots\ldots\ldots\; N\left\{\begin{matrix}A\\A\\A\\A\end{matrix}\right\}Cl$$

are even more easily prepared and more frequently met with.

This synopsis shows that the number of salts capable of being derived from the ordinary ammoniacal salts, must be very considerable. Even now a very extensive series has been prepared, although the number of radicals at our disposal at present is still comparatively limited.

It has been mentioned that all attempts at isolating both ammonium and its oxides have hitherto failed (see page 232). On treating chloride of ammonium or sulphate of ammonia with mineral oxides, such as potassa, lime, and baryta, decomposition ensues, chloride of potassium or sulphate of potassa, &c., is formed, and the separated oxide of ammonium splits into ammonia-gas and water, $NH_4O=NH_3+HO$ (see page 162).

The compound ammonia salts are likewise decomposed by mineral oxides. With the three first classes the change is perfectly analogous to that of ammoniacal salts, the separated oxide is decomposed into water and a volatile base, the properties of which, according to the nature of the replacing radicals, are more or less closely approximated to those of ammonia itself. We arrive in this manner at three groups of organic bases, differing from one another by the amount of hydrogen which is replaced; they have been distinguished by the terms *amidogen-*, *imidogen-*, and *nitrile-bases.*

$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}A\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}A\\B\\H\end{matrix}\right.$	$N\left\{\begin{matrix}A\\B\\C\end{matrix}\right.$
Ammonia.	Amidogen-bases.	Imidogen-bases.	Nitrile-bases.

The last group of ammoniacal salts, in which the 4 eq. of hydrogen are replaced by radicals, differ in their deportment from the former classes. These salts are not decomposed by potassa, but yield, by appropriate treatment, a series of substances of a very powerfully alkaline character, which are expressed by the general formulæ:—

$$N\left\{\begin{matrix}A\\B\\C\\D\end{matrix}\right\}O,HO,$$

evidently analogous to hydrated oxide of ammonium; from which they er, however, in a remarkable manner, by their powerful stability.

'hese general statements will become more intelligible if we elucidate them the description of several individual substances; the limits of this work ıpel us, however, to confine ourselves to the more important members of ı already very numerous group, which is moreover daily increasing.

t may at once be stated that by far the greater number of these compounds derived from the alcohols or substances analogous to them, and that the icals which in the preceding sketch have been designated by the letters B, C, and D, are chiefly the hydrocarbons previously described under the nes *ethyl*, *methyl*, and *amyl*.

BASES OF THE ETHYL-SERIES.

Ethylamine, *Ethyl-ammonia*, $C_4H_7N = (H_2, C_4H_5) = N(H_2Ae)$.—On digest- bromide or iodide of ethyl (see page 353) with an alcoholic solution of monia, the alkaline reaction of the ammonia gradually disappears. On porating the solution on the water-bath a white crystalline mass is ained, which consists chiefly of bromide of ethyl-ammonium, $AeI + NH_3$ $N(H_3Ae)I$. On distilling this salt in a retort provided with a good con- ıser, with caustic lime, the ethylamine is liberated and distils over,

$$NH_2AeI + KO = N(H_2Ae) + HO + KI.$$

Another method of preparing this compound, and indeed the method by ich this remarkable substance was first obtained by M. Wurtz, consists in mitting cyanate of ethyl to the action of hydrate of potassa. In describ- cyanic acid (see page 426), the interesting change has been mentioned, ich this substance undergoes when treated with boiling solution of potassa. this case cyanic acid splits into 2 eq. of carbonic acid and 1 eq. of am- nia; cyanate of ethyl (see page 428) suffers a perfectly analogous decom- sition, and instead of ammonia we obtain ethylamine.

$$\underbrace{C_2NO,HO}_{\text{Hydrated cyanic acid.}} + 2(KO,HO) = 2(KO,CO_2) + NH_3$$

$$\underbrace{C_2NO,AeO}_{\text{Cyanate of ethyl.}} + 2(KO,HO) = 2(KO,CO_2) + \underbrace{N(H_2Ae)}_{\text{Ethylamine.}}$$

anurate of ethyl, isomeric with the cyanate, likewise furnishes ethylamine.

Ethylamine is a very mobile liquid of 0·6964 sp. gr., at 46°·4 (8°C), which ils at 64°·4 (18°C). The sp. gr. of the vapour is 1·57. It has a most werfully ammoniacal odour, and restores the blue colour to reddened mus paper. It produces white clouds, with hydrochloric acid, and is sorbed by water with great avidity. With the acids it forms a series of utral crystallizable salts perfectly analogous to those of ammonium.

This substance imitates, moreover, in a remarkable manner, the deport- nt of ammonia with metallic salts. It precipitates the salts of magnesia, mina, iron, manganese, bismuth, chromium, uranium, tin, lead, and mer- ry. Zinc-salts yield a white precipitate which is soluble in excess. Like monia, ethylamine dissolves chloride of silver, and yields with copper- lts a blue precipitate, which is soluble in an excess of ethylamine. On ding ethylamine to oxalic ether, a white precipitate of *ethyl-oxamide*. $HAe),C_2O_2$, is produced; even a compound analogous to oxamic acid (see e 348) has been obtained. Ethylamine may, however, be readily distin-

guished from ammonia; its vapour is inflammable; and it produces, with bichloride of platinum, a salt $N(H_3Ae)Cl,PtCl_2$, crystallizing in golden scales, which are rather soluble in water. If ethylamine is treated with chlorine, it furnishes chloride of ethyl-ammonium and a yellow liquid of a penetrating odour exciting tears, which contains NCl_2Ae. This substance is *bichlorethylamine*. When treated with potassa it is converted into ammonia, acetate of potassa, and chloride of potassium, $NCl_2,C_4H_5+3KO+HO=KO,C_4H_3O_3+NH_3+2KCl$.

Ethylamine-urea. On passing into a solution of ethylamine, the vapour of hydrated cyanic acid, the liquid becomes hot, and deposits after evaporation fine crystals of ethylamine-urea, $C_4H_7N+C_2NO,HO=C_6H_8N_2O_2=C_2(H_3,C_4H_5)N_2O_2=C_2(H_3Ae)N_2O_2$. This substance, which may be received as ordinary urea (see page 436), in which 1 eq. of hydrogen is replaced by ethyl, may be prepared also by treating cyanic ether with ammonia, $C_4H_5O,C_2NO+NH_3=C_6H_8N_2O_2$. Ethylamine urea is very soluble in water and alcohol; the concentrated aqueous solution, unlike that of ordinary urea, yields no precipitate with nitric acid; but on gently evaporating the mixture, a very soluble crystalline nitrate of ethylamine urea is obtained. Boiled with potassa, this substance yields a mixture of equal equivalents of ammonia and ethylamine, $C_2(H_3Ae)N_2O_2+2(KO,HO)=2(KO,CO_2)+NH_3+N(H_2Ae)$.

BIETHYLAMINE, *Biethyl-ammonia*, $C_8H_{11}N=NH,2C_4H_5=N(HAe_2)$.—A mixture of solution of ethylamine and bromide of ethyl, heated in a sealed tube for several hours, solidifies to a crystalline mass of bromide of biethyl-ammonium, $N(H_2Ae)+AeBr=N(H_2Ae_2)Br$. The bromide, when distilled with potassa, furnishes a colourless liquid, still very alkaline, and soluble in water, but less so than ethylamine. This compound boils at 183° (56°C). It forms beautifully crystallizable salts with acids. A solution of chloride of biethyl-ammonium furnishes with bichloride of platinum, a very soluble double salt, $N(H_2Ae_2)Cl,PtCl_2$, crystallizing in orange-red grains, very different from the orange-yellow leaves of the corresponding ethyl-ammonium salts.

Biethylamine-urea. Biethylamine probably behaves with cyanic acid like ammonia and ethylamine, giving rise to biethylamine-urea. This substance has been produced by the action of cyanic ether upon ethylamine, $C_4H_5O,C_2NO+C_4H_7N=C_{10}H_{12}N_2O_2=C_2(H_2,2C_4H_5)N_2O_2=C_2(H_2Ae_2)N_2O_2$. Biethylamine-urea is very crystallizable, and readily forms a crystalline nitrate. Boiled with potassa, biethylamine-urea yields pure ethylamine, $C_2(H_2Ae_2)N_2O_2+2(KO,HO)=2(KO,CO_2)+2N(H_2Ae)$.

TRIETHYLAMINE, *Triethyl-ammonia*, $C_{12}H_{15}N=N3C_4H_5=NAe_3$.—The formation of this body is perfectly analogous to those of ethylamine and biethylamine. On heating for a short time a mixture of biethylamine with bromide of ethyl in a sealed glass tube, a beautiful fibrous mass of bromide of triethyl-ammonium is obtained, from which the triethylamine is separated by potassa. Triethylamine is a colourless, powerfully alkaline liquid, boiling at 195°·8 (91°C). The salts of this base crystallize remarkably well. With bichloride of platinum it forms a very soluble double salt, $N(HAe_3)Cl,PtCl_2$, which crystallizes in magnificent large orange-red rhombs.

Hydrated Oxide of Tetrethyl-ammonium, $C_{16}H_{21}NO_2=N4(C_4H_5)O,HO=NAe_4O,HO$.—When anhydrous triethylamine is mixed with dry iodide of ethyl, a powerful reaction ensues, the mixture enters into ebullition, and solidifies on cooling to a white crystalline mass of iodide of tetrethyl-ammonium, $NAe_3+AeI=NAe_4I$. The new iodide is readily soluble in hot water, from which it crystallizes on cooling in beautiful crystals of considerable size. The substance is not decomposed by potassa; it may be boiled with the alkali for hours without yielding a trace of volatile base. The iodine may, however, be readily removed by treating the solution with silver-salts. If in that

sulphate or nitrate of silver be employed, we obtain together with iodide of silver, the sulphate or nitrate of oxide of tetrethyl-ammonium, which crystallize on evaporation; on the other hand, if the iodide be treated with freshly precipitated protoxide of silver, the oxide of tetrethyl-ammonium itself is separated. On filtering off the silver-precipitate, a clear colourless liquid is obtained, which contains the isolated base in solution. It is of a strongly alkaline reaction, and has an intensely bitter taste. Solution of oxide of tetrethyl-ammonium has a remarkable analogy to potassa and soda. Like the latter substance, it destroys the epidermis and saponifies fatty substances with formation of true soaps. With the salts of the metals, this substance exhibits exactly the same reactions as potassa. On evaporating a solution of the base *in vacuo*, long slender needles are deposited, which are evidently the hydrate of the base, with an additional amount of water of crystallization. After some time these needles disappear again, and a semi-solid mass is left, which is the hydrate of oxide tetrethyl-ammonium. A concentrated solution of this substance in water may be boiled without decomposition, but on heating the dry substance, it is decomposed into pure triethylamine and olefiant gas.

$$NAe_4O,HO = 2HO + NAe_3 + C_4H_4.$$

Oxide of tetrethyl-ammonium forms neutral-salts with the acids. They are mostly very soluble; several yield beautiful crystals. The platinum salt, $NAe_4Cl,PtCl_2$, forms orange-yellow octahedrons, which are of about the same solubility as the corresponding bichloride of platinum and potassium.

Oxide of tetrethyl-ammonium is obviously perfectly analogous to the hitherto hypothetical oxide of ammonium. It is a compound of remarkable stability, the existence and properties of which must be regarded as powerful supports of the ammonium-theory.

BASES OF THE METHYL-SERIES.

METHYLAMINE, *Methylammonia*, $C_2H_5N = N(H_2,C_2H_3) = N(H_2Me)$. — The formation and the method of preparing this compound from the cyanate of methyl, is perfectly analogous to those of ethylamine (see page 455); however, methylamine being a gas at the common temperature, it is necessary to cool the receiver by a freezing mixture. The distillate, which is an aqueous solution of methylamine, is saturated with hydrochloric acid, and evaporated to dryness. The crystalline residue, which is the chloride of methyl-ammonium, when distilled with dry lime, yields methylamine gas, which, like ammonia gas, has to be collected over mercury. It is distinguished from ammonia, by a slightly fishy odour, and by the facility with which it burns. Methylamine is liquefied about 32° (0°C), its sp. gr. is 1·08. This substance is the most soluble of all gases, at 53°·6 (12°C) 1 volume of water absorbs 1040 volumes of gas. It is likewise very readily absorbed by charcoal. In its chemical deportment with acids and other substances, methylamine resembles in every respect ammonia and ethylamine. Methylamine appears to be produced in a great number of processes of destructive distillation; it has been formed by distilling several of the natural organic bases, such as codeine, morphine, caffeine, and several others, with caustic potassa; frequently a mixture of several bases are produced in this manner.

Among the numerous derivatives already obtained with this substance, *methylamine-urea* $C_2(H_3Me)N_2O_2$, and *bimethylamine-urea* $C_2(H_2Me_2)N_2O_2$, and even a *methyl-ethylamine-urea* $C_2(H_2MeAe)N_2O_2$ may be quoted. The latter substance has been produced by the action of cyanate of ethyl upon methylamine. *Even a series of* platinum-bases analogous to those produced by the

$H_5N_2O_2 = C_2(H_3Ae)N_2O_2$. This substance, urea (see page 436), in which 1 eq. of H be prepared also by treating cyanic eth $= C_6H_8N_2O_2$. Ethylamine urea is ve concentrated aqueous solution, unlike cipitate with nitric acid; but on soluble crystalline nitrate of ethyl tassa, this substance yields a mix ethylamine, $C_2(H_3Ae)N_2O_2 + 2(H$

BIETHYLAMINE, *Biethyl-ammo* ture of solution of ethylamine for several hours, solidifies ammonium, $N(H_2Ae) + AeB$ with potassa, furnishes a c water, but less so than e It forms beautifully cry of biethyl-ammonium f double salt, $N(H_2Ae_2)C$ rent from the orange salts.

Biethylamine-urea ammonia and eth has been produc $C_2NO + C_4H_7N =$ mine-urea is v Boiled with p $O_2 + 2(KO,H$

TRIETHYL mation of t thylamine. bromide o of triethy rated by

resent $_8H_8NO$ be obtain th substances ed, however, wi th an alcoholic sol iodides of ammoni thyl-ammonium, and and last compound form ystallization, the iodide of soluble in water. From the of protoxide of silver. The responding ethyl-compound. It tri-ammonium in its behaviour does trimethylamine, and pure met

SES OF THE AMYL-SERIES.

bodies being perfectly analogous to the ethyl-series, we refer to the more c and confine ourselves to a brief observ

monia, $C_{10}H_{13}N = N(H_2,C_{10}H_{11}) = N(H_2$ liar penetrating aromatic odour, sligh imparts a strongly alkaline reaction. Wit salts, which have a fatty lustre. Amylan

has been prepared.

amyl-ammonia, $C_{20}H_{23}N = N(H,2C_{10}H_{11}) = N$ soluble in water, and less alkaline than an (170°C).

THE PHENYL-SERIES.

$H_2,C_{12}H_5) = N(H_2Pyl)$. — Under the
so page 399), a volatile crystal-
hydrated oxide of phenyl.
n in Section IX., imitates
ut several very character-
lly the conversion into the
zed. The organic base, how-
e same manner as methylamine,
ethyl-, and amyl-alcohol, is known
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yet been obtained. However, on heating
sealed tubes, aniline is produced, PylO,HO
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ion of aniline and phenyl-alcohol, is not calcu-
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ed with a highly-concentrated solution of hydrate of
evolution of hydrogen gas to a brownish-red liquid
r acid, the *chrysanilic*, which becomes gradually converted
, the *anthranilic* (see page 474). If this matter be trans-
t and still farther heated, it swells up and disengages ani-
idenses in the form of oily drops in the neck of the retort and
. Separated from the ammoniacal water by which it is accom-
-distilled, it is obtained nearly colourless. The formation of
ndigo is represented by the following equation :—

$$\underbrace{NO_2}_{\text{go.}}+2(KO,HO)+2HO=\underbrace{C_{12}H_7N}_{\text{Aniline.}}+4(KO,CO_2)+4H.$$

prepare aniline from nitrobenzol (see page 399), this substance
a process discovered by Zinin, which has proved a very abun-
artificial organic bases. An alcoholic solution of nitro-benzol
ammonia and sulphuretted hydrogen, until after some hours a
sulphur takes place. The brown liquid is now saturated again
tted hydrogen, and the process repeated until sulphur is no
ed. The reaction may be remarkably accelerated by occasion-
r distilling the mixture. The liquid is then mixed with excess
id, boiled to expel alcohol and unaltered nitrobenzol, and then
excess of caustic potassa. The transformation of nitrobenzol
represented by the equation :—

$$\underbrace{C_{12}H_5NO_4}_{\text{Nitrobenzol.}}+6HS=\underbrace{C_{12}H_7N}_{\text{Aniline.}}+4HO+6S$$

e be required quite pure, it must be converted into oxalate, the
nes crystallized from alcohol, and again decomposed by hydrate

ts among the products of the distillation of coal, and probably
ic matters ; it is formed in the distillation of anthranilic acid
, and occasionally in other reactions.
aniline forms a thin, oily, colourless liquid, of faint vinous

action of ammonia upon protochloride of platinum (see page 309), have been obtained with methylamine.

BIMETHYLAMINE has not yet been prepared in a pure state.

TRIMETHYLAMINE, *trimethyl-ammonia*, $C_6H_9N = N3C_2H_3 = NMe_3$. — This substance is readily obtained in a state of perfect purity, by submitting oxide of tetramethyl-ammonium (see the following compound) to the action of heat. It is gaseous at the common temperature, but liquefies at about 46°·2 (8°C) to a mobile fluid of very powerfully alkaline reaction. Trimethylamine produces with acids very soluble salts. The platinum-salt $N(HMe_3)Cl,PtCl_2$, is likewise very soluble and crystallizes in splendid orange-red octahedrons. According to Mr. Winkles, large quantities of trimethylamine are found in the liquor in which salt herrings are preserved.

HYDRATED OXIDE OF TETRAMETHYL-AMMONIUM, $C_8H_{13}NO_2 = N4C_2H_3,O,HO = NMe_4O,HO$. — The corresponding iodide may be obtained by adding iodide of methyl to the preceding compound. Both substances unite with a sort of explosion. The same iodide is prepared, however, with less difficulty, simply by digesting iodide of methyl with an alcoholic solution of ammonia. In this reaction, a mixture of the iodides of ammonium, methyl-ammonium, bimethyl-ammonium, trimethyl-ammonium, and tetramethyl-ammonium is produced. The first and last compound form in largest quantity, and may be separated by crystallization, the iodide of tetramethyl-ammonium being rather difficultly soluble in water. From the iodide the base itself is separated by means of protoxide of silver. The properties are similar to those of the corresponding ethyl-compound. It differs, however, from oxide of tetrethyl-ammonium in its behaviour when heated (see page 457), yielding as it does trimethylamine, and pure methyl-alcohol, $NMe_4O,HO = NMe_3 + MeO,HO$.

BASES OF THE AMYL-SERIES.

The formation of these bodies being perfectly analogous to that of the corresponding terms in the ethyl-series, we refer to the more copious statement given in page 455, and confine ourselves to a brief observation of their principal properties.

AMYLAMINE, *amyl-ammonia*, $C_{10}H_{13}N = N(H_2,C_{10}H_{11}) = N(H_2Ayl)$, colourless liquid of a peculiar penetrating aromatic odour, slightly soluble in water, to which it imparts a strongly alkaline reaction. With the acids it forms crystalline salts, which have a fatty lustre. Amylamine boils at 199°·4 (93°C).

An *amylamine-urea* has been prepared.

BIAMYLAMINE, *biamyl-ammonia*, $C_{20}H_{23}N = N(H,2C_{10}H_{11}) = N(HAyl_2)$, aromatic liquid, less soluble in water, and less alkaline than amylamine. It boils at about 338° (170°C).

TRIAMYLAMINE, *triamyl-ammonia*, $C_{30}H_{33}N = N3C_{10}H_{11} = NAyl_3$, colourless liquid of properties similar to those of the two preceding bases, but boiling at 494°·6 (257°C). The salts of triamylamine are very insoluble in water, and fuse, when heated, to colourless liquids, floating upon water.

HYDRATED OXIDE OF TETRAMYL-AMMONIUM, $C_{40}H_{45}NO_2 = N4C_{10}H_{11},O,HO = NAyl_4O,HO$. — This substance is far less soluble than the corresponding bases of the methyl- and ethyl-series. On adding potassa to the aqueous solution the compound separates as an oily layer. On evaporating the solution in an atmosphere free from carbonic acid, the alkali may be obtained in splendid crystals of considerable size. When submitted to distillation it splits into water, triamylamine, and amylene (see page 390), $NAyl_4O,HO = 2HO + NAyl_3 + C_{10}H_{10}$.

BASES OF THE PHENYL-SERIES.

ANILINE, *phenylamine*, $C_{12}H_7N = N(H_2,C_{12}H_5) = N(H_2Pyl)$. — Under the head of salicylic acid (see page 406, and also page 399), a volatile crystalline substance has been noticed by the name of hydrated oxide of phenyl. This substance, of which a fuller description is given in Section IX., imitates to a certain extent the deportment of an alcohol, but several very characteristic transformations of the alcohols, and especially the conversion into the corresponding acid, have not as yet been realized. The organic base, however, which is derived from this alcohol in the same manner as methylamine, ethylamine, and amylamine, from methyl-, ethyl-, and amyl-alcohol, is known under the term *aniline*, a name given to it on account of its relation to the indigo-series. Aniline cannot be produced from phenyl-alcohol by the same processes which have furnished the bases of the other alcohols, neither bromide nor iodide of phenyl having as yet been obtained. However, on heating phenyl-alcohol with ammonia in sealed tubes, aniline is produced, $PylO,HO + NH_3 = 2HO + N(H_2Pyl)$. This process, however, although interesting as establishing clearly the relation of aniline and phenyl-alcohol, is not calculated to yield large quantities of this substance. Aniline is invariably obtained either from indigo or from nitrobenzol.

Powdered indigo boiled with a highly-concentrated solution of hydrate of potassa dissolves with evolution of hydrogen gas to a brownish-red liquid containing a peculiar acid, the *chrysanilic*, which becomes gradually converted into another acid, the *anthranilic* (see page 474). If this matter be transferred to a retort and still farther heated, it swells up and disengages aniline, which condenses in the form of oily drops in the neck of the retort and in the receiver. Separated from the ammoniacal water by which it is accompanied, and re-distilled, it is obtained nearly colourless. The formation of aniline from indigo is represented by the following equation :—

$$\underbrace{C_{16}H_5NO_2}_{\text{Indigo.}} + 2(KO,HO) + 2HO = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + 4(KO,CO_2) + 4H.$$

In order to prepare aniline from nitrobenzol (see page 399), this substance is submitted to a process discovered by Zinin, which has proved a very abundant source of artificial organic bases. An alcoholic solution of nitro-benzol is treated with ammonia and sulphuretted hydrogen, until after some hours a precipitate of sulphur takes place. The brown liquid is now saturated again with sulphuretted hydrogen, and the process repeated until sulphur is no longer separated. The reaction may be remarkably accelerated by occasionally heating or distilling the mixture. The liquid is then mixed with excess of acid, filtered, boiled to expel alcohol and unaltered nitrobenzol, and then distilled with excess of caustic potassa. The transformation of nitrobenzol into aniline is represented by the equation :—

$$\underbrace{C_{12}H_5NO_4}_{\text{Nitrobenzol.}} + 6HS = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + 4HO + 6S$$

If the aniline be required quite pure, it must be converted into oxalate, the salt several times crystallized from alcohol, and again decomposed by hydrate of potassa.

Aniline exists among the products of the distillation of coal, and probably of other organic matters ; it is formed in the distillation of anthranilic acid (see page 474), and occasionally in other reactions.

When pure, aniline forms a thin, oily, colourless liquid, of faint vinous

odour, and aromatic, burning taste. It is very volatile, but nevertheless has a high boiling-point, 359°·6 (182°C). In the air it gradually becomes yellow or brown, and acquires a resinous consistence. Its density is 1·028. Water dissolves aniline to a certain extent, and also forms with it a kind of hydrate; alcohol and ether are miscible with it in all proportions. It is destitute of alkaline reaction to test-paper, but is quite remarkable for the number and beauty of the crystallizable compounds it forms with acids. Two extraordinary reactions characterize this body and distinguish it from all others, viz., that with chromic acid, and that with solution of hypochlorite of lime. The former gives with aniline a deep greenish- or bluish-black precipitate, and the latter an extremely beautiful violet-coloured compound, the fine tint of which is, however, very soon destroyed.

Substitution-products of aniline. — Under the head of indigo, a product of oxidation of this substance will be noticed, to which the name isatin has been given (see page 471). When isatin is distilled with an exceedingly concentrated solution of caustic potassa, it is, like indigo, resolved into aniline, carbonic acid, and free hydrogen. In like manner, when *chlorisatin* or *bichlorisatin*, two chloro-substitutes of isatin, are similarly treated, they yield products analogous to aniline, but containing one or two equivalents of chlorine respectively in place of hydrogen. The *chloraniline*, $C_{12}(H_6Cl)N$, and *bichloraniline*, $C_{12}(H_5Cl_2)N$, thus produced, cannot be obtained directly, however, from aniline by the action of chlorine, thus differing from ordinary substitution-compounds; but aniline may be reproduced from them by the same re-agent, which is capable of reconverting chloracetic acid into ordinary acetic acid, namely, an amalgam of potassium (see page 375). They are the first cases on record of organic bases containing chlorine.

Chloraniline forms large, colourless octahedrons having exactly the odour and taste of aniline, very volatile, and easily fusible; it distils without decomposition at a high temperature, and burns, when strongly heated, with a red smoky flame with greenish border. It is heavier than water, indifferent to vegetable colours, and, except in being solid at common temperatures, resembles aniline in the closest manner. It forms numerous and beautiful crystallizable salts. If aniline be treated with chlorine-gas, the action goes farther, *trichloraniline*, $C_{12}(H_4Cl_3)N$, being produced, a volatile crystalline body which has no longer any basic properties. The corresponding bromine-compounds have also been formed and described.

Nitraniline. — If nitrobenzol be heated with fuming nitric acid, or, still better, with a mixture of that acid and oil of vitriol, it is converted into a substance called *binitrobenzol*, containing $C_{12}H_4N_2O_8$, or nitrobenzol in which an additional equivalent of hydrogen is replaced by the elements of hyponitric acid (see page 399). When this is dissolved in alcohol and subjected to the reducing action of sulphide of ammonium in Zinin's process, it furnishes a new substance of basic properties, *nitraniline*, having the constitution of a hyponitric acid substitution-product of ordinary aniline. The attempts to prepare it direct from aniline by means of nitric acid were unsuccessful, the principal product being usually carbazotic acid. Nitraniline forms yellow, acicular crystals, but little soluble in cold water, although easily dissolved by alcohol and ether. When warmed it exhales an aromatic odour, and melts. At a higher temperature it distils unchanged. By very gentle heat it may be sublimed without fusion. It is heavier than water, does not affect test-paper, and like chlor- and bromaniline fails to give with hypochlorite of lime the characteristic reaction of the normal compound. Nitraniline forms crystallizable salts, of which the hydrochlorate is the best known. This substance contains the elements of aniline with an equivalent of hydrogen replaced by hyponitric acid, or $C_{12}H_6N_2O_4 = C_{12}(H_6NO_4)N$.

Cyaniline is formed by the action of cyanogen upon aniline; it is a cry-

lline substance capable of combining with acids like aniline, but very prone decomposition. Cyaniline contains $C_{14}H_7N_2 = C_{12}H_7NCy$. Hence it is rmed by the direct union of 1 eq. of cyanogen and 1 eq. of aniline.

Melaniline.—The action of dry chloride of cyanogen upon anhydrous anile gives rise to the formation of a resinous substance, which is the chlorae-compound of a very peculiar basic substance to which the name meailine has been given. Dissolved in water and mixed with potassa, the ove salt furnishes melaniline in form of an oil, which rapidly solidifies to beautiful crystalline mass. Melaniline contains $C_{26}H_{13}N_3$. The following uation represents its formation:—

$$2C_{12}H_7N + C_2NCl = C_{26}H_{14}N_3Cl.$$

Melaniline, when treated with chlorine, bromine, iodine, or nitric acid, lelds basic substitution-products, in which invariably 2 eq. of hydrogen are replaced. It combines with 2 eq. of cyanogen.

The constitution of the substitution-products of aniline is readily intellible; it is evident that these substances owe their origin to a double substitution, namely, first, of 1 equivalent of hydrogen in ammonia by phenyl; ad, secondly, of one or several equivalents of hydrogen in phenyl by hlorine, bromine, &c. The arrangement of the elements may be convenintly illustrated by the following formulæ:—

Ammonia	NH_3
Aniline	$NH_2,C_{12}H_5$
Chloraniline	$NH_2,C_{12}(H_4Cl)$
Bromaniline	$NH_2,C_{12}(H_4Br)$
Bibromaniline	$NH_2,C_{12}(H_3Br_2)$
Tribromaniline	$NH_2,C_{12}(H_2Br_3)$
Nitraniline	$NH_2,C_{12}(H_4NO_4)$

le constitution of cyaniline and melaniline is not so readily understood.

Aniline-compounds corresponding to the amides and amidogen-acids, &c.—In scribing the ammonia-salts of various acids, attention has been repeatedly lled to the power possessed by many of them to yield several new groups compounds by the loss of a certain amount of water (see pages 343 and 5). These groups are perhaps best elucidated by the derivatives of oxalic id.

$$\underbrace{NH_4O,C_2O_3}_{\text{Neutral oxalate of ammonia.}} \quad - \quad 2HO \quad = \quad \underbrace{C_2O_2N_2H}_{\text{Oxamide.}}$$

$$\underbrace{NH_4O,C_2O_3,HO,C_2O_3}_{\text{Binoxalate of ammonia.}} \quad - \quad 2HO \quad = \quad \underbrace{C_2O_2,NH_2C_2O_3,HO}_{\text{Oxamic acid.}}$$

$$\underbrace{NH_4O,C_2O_3}_{\text{Neutral oxalate of ammonia.}} \quad - \quad 4HO \quad = \quad \underbrace{C_2N}_{\text{Oxalonitrile or cyanogen.}}$$

The terms corresponding to oxamide and oxamic acid have also been obined in the aniline-series; they are produced by the distillation of neutral d acid oxalate of aniline, and have been called *oxanilide* and *oxanilic acid*.

$$\text{Oxanilide} = C_{14}H_6NO_2 = C_2O_2,N(HPyl)$$
$$\text{Oxanilic acid} = C_{16}H_8NO_6 = C_2O_2,N(HPyl),C_2O_3,HO.$$

Compounds analogous to the nitriles have not been obtained in the aniline-

series, and the reason is intelligible if we glance at the formula of oxalate of aniline, $N(H_2Pyl)O,C_2O_3$. It is obvious that 4 eq. of water cannot be eliminated from this salt without touching the hydrogen of the phenyl, i.e., without destroying the compound altogether. A great many anilides and anilic acids have been formed.

Aniline-urea.—On passing the vapour of cyanic acid into aniline, the substance becomes hot, and solidifies on cooling to a crystalline mass, containing $C_{14}H_8N_2O_2 = C_2(H_3Pyl)N_2O_2$. This is the composition of aniline-urea. The substance, however, does not combine with acids like the ureas (see pages 427 and 450), it is only isomeric with the true aniline-urea, which is obtained by another process. Among the derivatives of benzoic-acid, nitrobenzoic acid, $C_{14}(H_4NO_4)O_3,HO$, (see page [illegible]) has been mentioned. The ether of this acid, $C_4H_5O,C_{14}(H_4NO_4)O_3$, like oxalic ether, and many other ethers, furnishes an amide when treated with ammonia. This substance, nitrobenzamide, $C_{14}(H_4NO_4)O_2,NH_2$, under the influence of sulphide of ammonium suffers a change, which is perfectly analogous to that of nitrobenzol under similar conditions (see page 450). The mixture soon deposits sulphur, and yields, on evaporation, crystals of aniline-urea.

$$\underbrace{C_{14}H_6N_2O_6}_{\text{Nitrobenzamide.}} + 6HS = \underbrace{C_{14}H_8N_2O_2}_{\text{Aniline-urea.}} + 4HO + 6S$$

This substance, which was discovered by M. Chancel, combines with nitric and hydrochloric acid, and even with bichloride of platinum.

Bases homologous to Aniline.

In a former section of this Manual (page 406), a series of hydrocarbons has been mentioned, which are homologous to benzol. Each of these substances, when treated with fuming nitric acid, yields a nitro-substitute corresponding to nitrobenzol, which, under the influence of sulphuretted hydrogen, is converted into a basic compound homologous to aniline. We thus obtain the following group:—

Benzol.	$C_{12}H_5H$	Nitrobenzol.	$C_{12}H_5NO_4$	Aniline.	$N(H_2,C_{12}H_5)$
Toluol.	$C_{14}H_7H$	Nitrotoluol.	$C_{14}H_7NO_4$	Toluidine.	$N(H_2,C_{14}H_7)$
Xylol.	$C_{16}H_9H$	Nitroxylol.	$C_{16}H_9NO_4$	Xylidine.	$N(H_2,C_{16}H_9)$
Cumol.	$C_{18}H_{11}H$	Nitrocumol.	$C_{18}H_{11}NO_4$	Cumidine.	$N(H_2,C_{18}H_{11})$

TOLUIDINE, $C_{14}H_9N = N(H_2,C_{14}H_7) = N(H_2,Tyl)$. — This is prepared exactly like aniline.

Toluidine forms colourless plate crystals, very sparingly soluble in water, but easily in alcohol, ether, and oils: it is heavier than water, has an aromatic taste and odour, and a very feeble alkaline reaction. At 104° (40°C) it melts, and at 388° (198°C), boils, and distils unchanged; it forms a series of beautiful crystallizable salts.

XYLIDINE, $C_{16}H_{11}N = N(H_2,C_{16}H_9) = N(H_2,Xyl)$. — Of this compound little more than the existence is known.

CUMIDINE, $C_{18}H_{13}N = N(H_2,C_{18}H_{11}) = N(H_2,Cyl)$. — This substance is an oil which boils at 437° (225°C). It forms magnificent salts with the acids.

The following two bases are likewise closely allied to the group of aniline-bases, both by their mode of formation and by their constitution.

NAPHTHALIDINE, $C_{20}H_9N = N(H_2,C_{20}H_7) = N(H_2,Nyl)$. — This substance is interesting, as being one of the first of its kind produced by Zinin's process. It is obtained by the action of sulphide of ammonium upon an alcoholic solution of nitronaphthalin, one of the numerous products of the action of nitric acid upon the hydrocarbon naphthalin, which will be noticed in the last section of the Manual. When pure it forms colourless silky needles,

sible, and volatile without decomposition. It has a powerful, not disagreeable odour and burning taste, is nearly insoluble in water, but readily dissolves in alcohol and ether; the solution has no alkaline reaction. Naphthalidine forms numerous crystallizable salts.

CHLORONICINE, $C_{10}(H_6Cl)N{=}NH_2C_{10}(H_4Cl)$. — A substance of the above composition has been lately discovered by Saint Evre, and deserves special notice, because it may be viewed as a chloro-substitute of the natural alkaloid nicotine (see page 450), which contains $C_{10}H_7N$. It is obtained by the following rather complicated series of reactions. A stream of chlorine is passed through a solution of benzoate of potassa to which some free alkali has been added, when a deposit forms consisting of chlorate of potassa and the potassa-salt of a new chlorinetted acid $C_{12}(H_4Cl)O_3,HO$. This acid, which is derived from benzoic acid by the removal of 2 eq. of carbon in the form of carbonic acid and by the introduction of 1 eq. of chlorine in the place of 1 eq. of hydrogen, has received the name of *chloroniceic acid*. It forms cauliflower-like crystals, fusible at 302° (150°C), and boiling at 419° (215°C). It is volatile without decomposition; when submitted to distillation with lime it yields a chlorinetted hydrocarbon chloronicene $C_{10}(H_6Cl)$, which is converted into *nitrochloronicene* $C_{10},(H_4ClNO_4)$ by the action of fuming nitric acid. This, lastly, when treated with sulphide of ammonium furnishes *chloronicine*. It forms brown flakes, which dissolve in a great deal of water; the solution, however, has no alkaline reaction. It forms crystallizable salts with hydrochloric and acetic acids, and a fine platinum-salt. The perfect analogy in the derivatives from chloroniceic acid to that of aniline and benzoic acid, is obvious from the following table:—

Benzoic acid	$C_{14}H_6O_4$	Chloroniceic acid	$C_{12}(H_5Cl)O_4$
Benzol	$C_{12}H_6$	Chloronicene	$C_{10}(H_5Cl)$
Nitrobenzol	$C_{12}(H_5NO_4)$	Nitrochloronicene	$C_{10}(H_4ClNO_4)$
Aniline	$C_{12}H_5,H_2N$	Chloronicine	$C_{10}(H_4Cl)H_2N$.

Up to the present moment chloronicine has not yet been converted into nicotine, nor has nicotine been transformed into chloronicine.

MIXED BASES.

In one of the preceding paragraphs it has been mentioned that the several hydrogen-equivalents in ammonium may be replaced by *different* hydro-carbon radicals. In fact, on treating aniline or toluidine with bromide, or iodide of ethyl, as described under the head of ethylamine, the following series of compounds are obtained:

Aniline	$N(H_2Pyl)$	Toluidine	$N(H_2Tyl)$
Ethylaniline	$N(HPylAe)$	Ethylotoluidine	$N(HTylAe)$
Biethylaniline	$N(PylAe_2)$	Biethylotoluidine	$N(TylAe_2)$
Ammonium base	$N(PylAe_3)O,HO$	Ammonium-base[1]	$N(TylAe_3)O,HO$

ETHYLANILINE (ethylophenylamine) and BIETHYLANILINE (biethylophenylamine) are liquids greatly resembling aniline. They boil respectively at 399°·2 (204°C) and 416°·5 (213°·5C). The ammonium-base, to which the name *Oxide of biethylophenyl-ammonium* may be given, is soluble in water, with a powerful alkaline reaction, corresponding in its general properties to oxide of tetrethyl-ammonium (see page 456). The series of bases which may be possibly obtained by changing the radicals is almost without limit; even now a considerable variety has been produced, of which however only

[1] *Unpublished researches* of Messrs R. Morley and John Abel.

a few will be mentioned here, as remarkable for the diversity of the materials with which they are constructed.

Hydrated oxide of triethylamyl-ammonium, $C_{26}H_{28}NO_2 = N(3C_4H_5, C_{10}H_{11})O,HO = N(Ae_3Ayl)O,HO$. Triethylamine (see page 456), when treated with iodide of amyl is slowly converted into a crystalline mass of iodide of *Triethylamyl-ammonium*. The base liberated with protoxide of silver and submitted to distillation yields olefiant gas, and

Biethylamylamine, $C_{18}H_{21}N = N(2C_4H_5, C_{10}H_{11}) = N(Ae_2Ayl)$, a liquid boiling at 309°·2 (154°C). This compound is most powerfully attacked by iodide of methyl. Both substances immediately solidify to a beautifully crystalline iodide from which protoxide of silver separates.

Hydrated oxide of methylo-biethylamyl-ammonium, $C_{20}H_{25}NO_2 = N(C_2H_3, 2C_4H_5, C_{10}H_{11})O,HO = N(MeAe_2Ayl),O,HO$. This substance, which is a powerfully alkaline base, soluble in water, when distilled undergoes the same decomposition as the other members of the fourth group of bases, yielding olefiant gas, and

Methylethylamylamine, or ammonia, in which 1 eq. of hydrogen is replaced by methyl, another by ethyl, and a third by amyl, $C_{16}H_{19}N = N(C_2H_3, C_4H_5, C_{10}H_{11}) = N(MeAeAyl)$. This is a basic oil of a peculiar aromatic odour, boiling at 275° (135°C) and forming crystallizable salt with the acids.

Ethylamylaniline, $C_{26}H_{21}N = N(C_{12}H_5, C_4H_5, C_{10}H_{11}) = N(PylAeAyl)$. — Ethylaniline (see page 463) treated with iodide of amyl yields the iodide of the above base, which is separated by distillation with potassa. It is an aromatic oil, boiling at 503°·5 (262°C). The action of iodide of methyl upon this substance gives rise to a new iodide from which protoxide of silver separates, and

Hydrated oxide of methyl-ethyl-amylo-phenyl-ammonium, $C_{28}H_{25}NO_2 = N(C_2H_3, C_4H_5, C_{10}H_{11}, C_{12}H_5)O,HO = N(MeAeAylPyl)O,HO$. This compound is very soluble in water, is powerfully alkaline, and of an extremely bitter taste. The composition, established by the examination of a platinum-salt, is certainly remarkable, for this compound contains the radicals of not less than four different alcohols.

BASES OF UNCERTAIN CONSTITUTION

In addition to the artificial bases which have just been described, several others have been formed by processes less simple and less calculated to afford a clear insight into their constitution. The destructive distillation of nitrogenous substances has furnished a rich harvest of similar substances. A few of the most interesting may be briefly mentioned.

Chinoleine (Leucoline) $C_{18}H_8N$. — Quinine, cinchonine, strychnine, and probably other bodies of this class, when distilled with a very concentrated solution of potassa, yield an oily product resembling aniline in many respects, and possessing strong basic powers; it is, however, less volatile than that substance, and boils at 460° (235°C). When pure it is colourless and has a faint odour of bitter almonds. Its density is 1·081. It is slightly soluble in water, and miscible in all proportions with alcohol, ether, and essential oils. Chinoleine has no alkaline reaction, but forms salts with acids, which, generally speaking, do not crystallize very freely.

Bases from Coal-tar Oil.

KYANOL and LEUKOL. — The volatile basic bodies described under these names have lately been identified, the first with aniline and the second with chinoleine. They are separated from the coal-oil by agitating large quantities of that liquid with hydrochloric or diluted sulphuric acid, and then distilling the acid liquid with excess of potassa or lime. They are readily separated by distillation.

PICOLINE $C_{12}H_7N$.—Dr. Anderson has described under the foregoing name a third volatile, oily base, present in certain varieties of coal-tar-naphtha, being there associated with aniline, chinoleine, and several other volatile substances but imperfectly understood. It is separated without difficulty from the two bases mentioned by distillation, in virtue of its superior volatility. Picoline, when pure, is a colourless, transparent, limpid liquid, of powerful and persistent odour, and acrid, bitter taste. It is unaffected by a cold of 0° (—17°·7C). It is extremely volatile, evaporates rapidly in the air, and does not become brown like aniline when kept in an ill-stopped bottle. Picoline has a sp. gr. of 0·955, and boils at 272° (133°·3C). It mixes in all proportions with pure water, but is insoluble in caustic potassa and most saline solutions. The alkalinity of this substance is exceedingly well marked; it restores the blue colour of reddened litmus, and forms a series of crystallizable salts. This substance, as seen from the above formula, is isomeric with aniline, but numerous characteristic reactions completely distinguish it from this body.

Bases from Animal Oil.

The oily liquid obtained by the distillation of bones and animal matter generally, frequently designated by the term Dippel's oil, contains several volatile organic bases. Together with some of the substances already described, such as methylamine, ethylamine, picoline, and analine, Dr. Anderson has found in it a peculiar base.

PETININE $C_8H_{11}N$.—The properties of this substance are very analogous to those of biethylamine, and triethylamine. It has the same composition as biethylamine, but differs from it by its higher boiling-point, which is 175° (79°·5C), that of biethylamine being 133° (55°C) (see page 455). Some chemists are inclined to explain this difference by assuming that petinine is an ammonia-base, containing the radical *butyl*, which was mentioned under the head of valeric acid (see page 392), in one word that it is *butylamine* $N(H_2, C_8H_9)$, homologous to ethylamine. This assumption may be correct, but is not as yet supported by any experimental evidence.

Bases obtained by the action of Ammonia upon Volatile Oils.

FURFURINE.—When sulphuric acid diluted with an equal bulk of water is carefully mixed with twice its weight of wheat-bran, and the adhesive pasty mass obtained exposed in a proper vessel to the action of a current of steam which is afterwards condensed by a worm or refrigerator, a liquid is obtained which holds in solution a peculiar volatile oil, to which the term *furfurole* has been given. By re-distillation several times repeated, the first half of the liquid only being collected, the furfurole can be extracted from the water, and then by distillation alone obtained in a state of purity. It has a pale yellow colour, and a fragrant odour like that of oil of cassia; its specific gravity is 1·165, and it boils at 325° (162°·8C), distilling unchanged. It dissolves in all proportions in alcohol and to a very considerable extent in water, and is readily destroyed by strong acids and caustic alkalis, especially when aided by heat. Furfurole contains $C_5H_2O_2$. The specific gravity of its vapour is 3·498.

When boiled with a somewhat dilute solutior
is disengaged, but the substance is slowly
be considerable, and the solution deposi
needles of a substance having the same c
There is no other product. This new b
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FUCUSINE.—By treating se
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THE ORGANIC BASES.

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Phosphorus-bases.

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Thénard, who has investiga
three compounds, containin
believes to correspond to th

a compound having the characters of an organic base, and forming .ess, prismatic crystals, bitter in taste and soluble in water. The n does not affect test-paper. It melts when heated, but cannot be ed. Acids combine with it, but form no crystallizable salts: the double f the hydrochlorate with bichloride of platinum and corrosive subli-re the most definite. This substance contains sulphur; its formula is $_{2}S_{2}$. It is the only product of the action of ammonia on the oil.

sinnamine is decomposed by metallic oxides, as protoxide of lead, roduction of a metallic sulphide and a new body of basic properties, om sulphur, called *sinnamine*. This latter substance crystallizes very from a concentrated aqueous solution in brilliant, colourless crystals contain water. It has a powerful bitter taste, is strongly alkaline to .per, and decomposes ammoniacal salts by boiling. With the excep- the oxalate, it forms no crystallizable salts. Sinnamine contains in rstallized state $C_8H_6N_2,HO$.

n mustard-oil is treated with protoxide of lead or baryta, the whole sulphur is withdrawn, and carbonic acid and another basic substance ed, which, when pure, crystallizes in colourless plates, soluble in water alcohol; the solution has a distinct alkaline reaction. *Sinapoline*, the o formed, contains $C_{14}H_{12}N_2O_2$.

Bases from Aldehyde.

ALDINE.—The crystalline compound of aldehyde with ammonia (see 69), is dissolved in 12 to 16 parts of water, mixed with a few drops of ammonia, and then the whole subjected to a feeble stream of sul-ted hydrogen. After a time the liquid becomes turbid and deposits a crystalline substance, which is the body in question. It is separated, d, dissolved in ether, and the solution mixed with alcohol and left to ate spontaneously, by which means the base is obtained in large, regu-ombic crystals, having the figure of those of common gypsum. The ls are heavier than water, transparent and colourless. They refract strongly. The substance has a somewhat aromatic odour, melts at 48°·3C), and volatilizes slowly at common temperatures. It distils ged with the vapour of water, but decomposes when heated alone. It sparingly soluble in water, easily in alcohol and ether. It has no on vegetable colours, but dissolves freely in acids, forming crystalli- salts. Heated with hydrate of lime it yields chinoleine. Thialdine is $C_{12}H_{13}NS_4$.

ry similar compound containing selenium exists.

NINE.—This substance is likewise obtained from aldehyde. It has only recently discovered by Strecker, who obtained it in a reaction, promises many interesting results. If an aqueous solution of the am- compound of aldehyde be treated with hydrocyanic and hydrochloric hloride of ammonium is formed, together with hydrochlorate of *ala-* On adding to this solution a mixture of alcohol and ether, the greater n of the chloride of ammonium is precipitated; the filtrate is then l with protoxide of lead to remove a small quantity of ammonium and hloric acid, and separated from the lead by sulphuretted hydrogen quid thus obtained deposits feathery crystals of alanine. The compo- of alanine is $C_6H_7NO_4$, and its formation represented by the equation:—

$$\underbrace{C_4H_4O_2}_{\text{Aldehyde.}} + \underbrace{HC_2N}_{\text{Hydrocyanic acid.}} + 2HO = \underbrace{C_6H_7NO_4}_{\text{Alanine.}}$$

-luble in water, and often used in dyeing;
compound analogous to sulphovinic
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gents, and with an alkali, indigo suffers a
es soluble and nearly colourless, perhaps re-
hich it existed in the plant. It is on this prin-
his *indigo-vat*:—5 parts of powdered indigo, 10
parts of hydrate of lime, and 60 parts of water, are
lose vessel, and then left to stand. The hydrated
njunction with the excess of lime, reduces the indigo
a yellowish liquid is produced, from which acids pre-
r *de-oxidized* indigo as a flocculent insoluble substance,
ygen with the greatest avidity, and becomes blue. Cloth
kaline liquid, and then exposed to the air, acquires a deep
nanent blue tint by the deposition of solid insoluble indigo in
of the fibre. Instead of the iron-salt and lime, a mixture of
c soda and grape-sugar dissolved in alcohol may be used; the
mes oxidized to formic acid, and the indigo reduced. On allowing
of this description to remain in contact with the air, it absorbs
and deposits the indigo in the crystalline condition.
following formulæ represent the composition of the bodies described:—

Blue insoluble indigo	$C_{16}H_5N\,O_2$
White, or reduced indigo[1]	$C_{16}H_6N\,O_2$
Sulphindylic acid	$C_{16}H_4N\,O,2SO_3,\,HO$.

Products of the Decomposition of Indigo.

he products of the destructive modification of indigo by powerful chemical
ts of an oxidizing nature are both numerous and interesting, inasmuch
ey connect this substance in a very curious manner with several other
ps of organic bodies, especially with those of the salicyl- and phenyl-
s. Many of them are exceedingly beautiful, and possess very remarkable
erties.

ATIN.—One part of indigo reduced to fine powder, and rubbed to a paste
water, is gently heated with a mixture of one part of sulphuric acid
one part of bichromate of potassa dissolved in 20 or 30 parts of water

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[1] operly *hydrogenised* indigo, if the above be the correct view; white indigo may, how be viewed as a *hydrate*, and blue indigo as an oxide, of one and the same substance.

White indigo	$C_{16}H^5N\,O+HO$
Blue indigo	$C_{16}H^5N\,O+O$

SECTION VI.

ORGANIC COLOURING PRINCIPLES.

The organic colouring principles are substances of very considerable practical importance in relation to the arts: several of them, too, have been made the subjects of extensive and successful chemical investigation. With the exception of one red dye, cochineal, they are all of vegetable origin.

The art of dyeing is founded upon an affinity or attraction existing between the colouring matter of the dye and the fibre of the fabric. In woollen and silk this affinity is usually very considerable, and to such tissues a permanent stain is very easily communicated, but with cotton and flax it is much weaker. Recourse is then had to a third substance, which does possess in a high degree such affinity, and with this the cloth is impregnated. Alumina, sesquioxide of iron, and oxide of tin are bodies of this class.

When an infusion of some dye-wood, as logwood, for example, is mixed with alum and a little alkali, a precipitate falls, consisting of alumina in combination with colouring matter, called a *lake*; it is by the formation of this insoluble substance within the fibre that a permanent dyeing of the cloth is effected. Such applications are termed *mordants*. Sesquioxide of iron usually gives rise to dull, heavy colours, alumina and oxide of tin, especially the latter, to brilliant ones. It is easy to see, that, by applying the mordant *partially* to the cloth, by a wood-block or otherwise, a pattern may be produced, as the colour will be removed by washing from the other portions.

INDIGO.

Indigo is the most important member of the group of blue colouring matters. It is the product of several species of the genus *indigofera*, which grow principally in warm climates. When the leaves of these plants are placed in a vessel of water and allowed to ferment, a yellow substance is dissolved out, which by contact of air becomes deep blue and insoluble, and finally precipitates. This, washed and carefully dried, constitutes the indigo of commerce. It is not contained ready-formed in the plant, but is produced by the oxidation of some substance there present. Neither is the fermentation essential, as a mere infusion of the plant in hot water deposits indigo by standing in the air.

Indigo comes into the market in the form of cubic cakes, which, rubbed with a hard body, exhibit a copper-red appearance; its powder has an intensely deep blue tint. The best is so light as to swim upon water. In addition to the blue colouring matter, or true indigo, it contains at least half its weight of various impurities, among which may be noticed a red resinous matter, the *indigo-red* of Berzelius; these may be extracted by boiling the powdered indigo in dilute acid, alkali, and afterwards in alcohol.

Pure indigo is quite insoluble in water, alcohol, oils, dilute acids, and alkalis; it dissolves in about 15 parts of concentrated sulphuric acid, forming

deep blue pasty mass, entirely soluble in water, and often used in dyeing; his is *sulphindylic or sulphindigotic acid*, a compound analogous to sulphovinic cid, capable of forming with alkaline bases blue salts, which, although easily oluble in pure water, are insoluble in saline solutions. If an insufficient uantity of sulphuric acid has been employed, or digestion not long enough ontinued, a purple powder is left on diluting the acid mass, soluble in a arge quantity of pure water. The Nordhausen acid answers far better for issolving indigo than ordinary oil of vitriol. Indigo may, by cautious mangement, be volatilized; it forms a fine purple vapour, which condenses in rilliant copper-coloured needles. The best method of subliming this subtance is, according to Mr. Taylor, to mix it with plaster of Paris, make the whole into a paste with water, and spread it upon an iron plate. 1 part inigo, and 2 parts plaster, answer very well. This, when quite dry, is heated y a spirit-lamp; the volatilization of the indigo is aided by the vapour of water disengaged from the gypsum, and the surface of the mass becomes overed with beautiful crystals of pure indigo, which may be easily removed y a thin spatula. At a higher temperature, charring and decomposition ake place.

In contact with de-oxidizing agents, and with an alkali, indigo suffers a ery curious change; it becomes soluble and nearly colourless, perhaps returning to the same state in which it existed in the plant. It is on this principle that the dyer prepares his *indigo-vat*:—5 parts of powdered indigo, 10 parts of green vitriol, 15 parts of hydrate of lime, and 60 parts of water, are agitated together in a close vessel, and then left to stand. The hydrated protoxide of iron, in conjunction with the excess of lime, reduces the indigo o the soluble state; a yellowish liquid is produced, from which acids precipitate the *white* or *de-oxidized* indigo as a flocculent insoluble substance, which absorbs oxygen with the greatest avidity, and becomes blue. Cloth steeped in the alkaline liquid, and then exposed to the air, acquires a deep and most permanent blue tint by the deposition of solid insoluble indigo in he substance of the fibre. Instead of the iron-salt and lime, a mixture of dilute caustic soda and grape-sugar dissolved in alcohol may be used; the sugar becomes oxidized to formic acid, and the indigo reduced. On allowing a solution of this description to remain in contact with the air, it absorbs oxygen and deposits the indigo in the crystalline condition.

The following formulæ represent the composition of the bodies described:—

Blue insoluble indigo	$C_{16}H_5N\,O_2$
White, or reduced indigo[1]	$C_{16}H_6N\,O_2$
Sulphindylic acid	$C_{16}H_4N\,O,2SO_3$, HO.

Products of the Decomposition of Indigo.

The products of the destructive modification of indigo by powerful chemical agents of an oxidizing nature are both numerous and interesting, inasmuch as they connect this substance in a very curious manner with several other groups of organic bodies, especially with those of the salicyl- and phenylseries. Many of them are exceedingly beautiful, and possess very remarkable properties.

Isatin.—One part of indigo reduced to fine powder, and rubbed to a paste with water, is gently heated with a mixture of one part of sulphuric acid and one part of bichromate of potassa dissolved in 20 or 30 parts of water

[1] Properly *hydrogenized* indigo, if the above be the correct view: white indigo may, however, be viewed as a *hydrate*, and blue indigo as an oxide, of one and the same substance.

White indigo	$C_{16}H^5N\ O+HO$
Blue indigo	$C_{16}H^5N\ O+O$

The indigo dissolves with very slight disengagement of carbonic acid towards the end, forming a yellow-brown solution, which on standing deposits impure *isatin* in crystals. These are collected, slightly washed and re-dissolved in boiling water; the filtered solution deposits on cooling the isatin in a state of purity. Or, powdered indigo may be mixed with water to a thin paste, heated to the boiling-point in a large capsule, and nitric acid added by small portions until the colour disappears; the whole is then largely diluted with boiling water, and filtered. The impure isatin which separates on cooling is washed with water containing a little ammonia, and re-crystallized. Both these processes require careful management, or the oxidizing action proceeds too far, and the product is destroyed.

Isatin forms deep yellowish-red prismatic crystals of great beauty and lustre; it is sparingly soluble in cold water, freely in boiling water, and also in alcohol. The solution colours the skin yellow, and causes it to emit a very disagreeable odour. It cannot be sublimed. Isatin contains the elements of indigo *plus* 2 eq. of oxygen, or $C_{16}H_5NO_4$.

A solution of potassa dissolves isatin with purple colour; from this solution acids precipitate the isatin unchanged. When boiled, however, the colour is destroyed, and the liquid furnishes on evaporation crystals of the potassa-salt of a new acid, the *isatinic*, containing $C_{16}H_6NO_5,HO$. In the free state this is a white and imperfectly crystalline powder, soluble in water, and easily decomposed into isatin and water.

By chlorine, isatin is converted into the substitution-product *chlorisatin*, $C_{16}(H_4Cl)NO_4$, a body closely resembling isatin itself in properties. If an alcoholic solution and excess of chlorine be employed, other products make their appearance, as *chloranile*, $C_{12}Cl_4O_4$, *trichlorophenol*, $C_{12}(H_3Cl_3)O_2$, and a resinous substance. The former of these substances, the position of which in the kinone-series has been already noticed (page 449), yields other products with potassa and ammonia. *Bromisatin* is easily formed. The changes which isatin, and its chlorinetted and brominetted congeners, undergo when submitted to the action of fusing hydrate of potassa has been already considered in the section on the vegeto-alkalis (see page 459).

Exposed to the action of sulphuretted hydrogen and sulphide of ammonium, isatin furnishes several new compounds, as *isathyde*, *sulfesathyde*, *sulfasathyde*.

A hot solution of isatin, when treated with sulphide of ammonium, gives rise to a deposit of sulphur, a white crystallized substance being produced at the same time; it has received the name of *isathyde*, and contains $C_{16}H_6NO_4$. It is obvious that it bears to isatin the same relation as white to blue indigo. If the sulphide of ammonium be replaced by sulphuretted hydrogen, *bisulphisathyde*, $C_{16}H_8NO_2S_2$, is produced, which is unlike the former: 2 eq. of oxygen, being replaced by 2 eq. of sulphur. An alcoholic solution of potassa converts this into *sulphisathyde*, $C_{16}H_6NO_3S$, in which only half of the oxygen in isatin is replaced by sulphur. Under the influence of cold aqueous solution of potassa, bisulphisathyde yields *indin*, $C_{16}H_6NO_2$, which is isomeric with white indigo. When treated with boiling potassa, indin fixes the elements of 2 eq. of water, and becomes indinic acid, $C_{16}H_7NO_3,HO$, the potassa-salt of which forms fine black needles.

Ammoniacal gas and solution of ammonia yield with isatin a series of interesting substances containing the nitrogen of the ammonia in addition to that of the isatin.

Action of chlorine on indigo. — In the dry state chlorine has no action whatever on indigo, even at the temperature of 212° (100°C). In contact with water, the blue colour is instantly destroyed, and cannot again be restored. The same thing happens with the blue solution of sulphindylic acid. When chlorine is passed into a mixture of powdered indigo and water and

colour disappears, and the product is then distilled in a retort, water [co]ntaining hydrochloric acid and a mixture of two volatile bodies, trichlor[ani]line, $C_{12}(H_4Cl_3)N$, and trichlorophenol, $C_{12}(H_3Cl_3)O_2$, pass over into the [rec]eiver, while the residue in the retort is found to contain chlorisatin, al[rea]dy mentioned, and *bichlorisatin*, $C_{16}(H_3Cl_2)NO_4$, much resembling that sub[sta]nce, but more freely soluble in alcohol. Both these bodies yield acids in [con]tact with boiling solution of potassa, by assimilating the elements of water. The action of bromine on indigo is very similar.

ANILIC AND PICRIC ACIDS.—Anilic or indigotic acid is prepared by adding [po]wdered indigo to a boiling mixture of 1 part of nitric acid and 10 parts [of] water, until the disengagement of gas ceases, filtering the hot dark-[co]loured liquid, and allowing it to stand. The impure anilic acid so ob[tai]ned is converted into the lead-salt, which is purified by crystallization and [th]e use of animal charcoal, and then decomposed by sulphuric acid. Anilic [ac]id forms fine white or yellowish needles, which have a feeble acid taste [an]d very sparing degree of solubility in cold water. In hot water and in [al]cohol it dissolves easily. It melts when heated, and on cooling assumes [a] crystalline structure. By careful management it may be sublimed un[ch]anged. Anilic acid contains $C_{14}H_4NO_9,HO{=}C_{14}(H_4NO_4)O_5,HO$. It has [be]en mentioned that the same acid is readily prepared from salicylic acid [(s]ee page 406). Hence it is more appropriately called *nitro-salicylic acid.*

Picric, carbazotic, or nitrophenisic acid, is one of the ultimate products [of] the action of nitric acid upon indigo and numerous other substances, as [si]lk, wool, several resins, especially that of *Xanthorhœa hastilis* (yellow gum [of] Botany Bay), salicin and some of its derivatives, cumarin, and certain [bo]dies belonging to the phenyl-series. It may be prepared from indigo by [ad]ding that substance in coarse powder and by small portions to ten or [tw]elve times its weight of boiling nitric acid of sp. gr. 1·43. When the last [of] the indigo has been added, and the action, at first extremely violent, has [be]come moderated, an additional quantity of nitric acid may be poured upon [th]e mixture, and the boiling kept up until the evolution of red fumes nearly [ce]ases. When cold, the impure picric acid obtained may be removed, con[ve]rted into potassa-salt, several times re-crystallized, and, lastly, decom[po]sed by nitric acid. In the pure state it forms beautiful pale yellow scaly [cr]ystals, but slightly soluble in cold water, and of insupportably bitter taste. [Pi]cric acid is used in dyeing; it forms a series of crystallizable salts of yel[lo]w or orange colour: that of potassa forms brilliant needles, and is so little [so]luble in cold water, that a solution of picric acid is occasionally used as a [pre]cipitant for that base. The alkaline salts of this acid explode by heat [wi]th extraordinary violence. The crystals of picric acid contain $C_{12}H_2N_3$ [...],HO.

If a solution of picric acid be distilled with hydrochlorite of lime, or a [mi]xture of chlorate of potassa and hydrochloric acid, an oily liquid of a [pen]etrating odour is obtained, having a sp. gr. of 1·665, and boiling between [23]7° and 239° (114° and 115°C). The substance, *chloropicrin*, was disco[ve]red by Stenhouse, who gives the formula $C_4Cl_7N_2O_{10}$; MM. Gerhardt and [La]urent assign to it the formula $C_2Cl_3NO_4$. According to the latter formula, [wh]ich is more probable, chloropicrin would be chloroform, in which the hy[dro]gen is replaced by the elements of hyponitric acid:

$$\text{Chloroform } C_2(HCl_3)\text{; Chloropicrin } C_2(NO_4Cl_3).$$

PRODUCTS OF THE ACTION OF HYDRATE OF POTASSA UPON INDIGO.—One of [th]e most remarkable of these, aniline, has been already described (see page [..]9). When powdered indigo is boiled with a very concentrated solution of [ca]ustic potassa, it is gradually dissolved with the exception of some brown[is]h flocculent matter, and the liquid on cooling deposits yellow crystals of

the potash-salt of a new acid, the chrysanilic, which can be procured in a purer state, by dissolving the crystals in water, filtering from reproduced indigo, and adding a slight excess of mineral acid. Chrysanilic acid can be obtained in indistinct crystals from weak alcohol; it is supposed to contain $C_{28}H_{12}N_2O_{10},HO$, but it is very probable that it is a mixture of several substances, especially isatinic acid.

When this substance is boiled with mineral acids, it is decomposed into another new acid, the anthranilic, which remains in solution, and a blue insoluble matter resembling indigo: a similar effect is slowly produced by the action of the air upon an alcoholic solution of chrysanilic acid. Anthranilic acid is colourless, sparingly soluble in cold water, easily soluble in alcohol. It melts when heated, sublimes under favourable circumstances, but decomposes entirely when heated in a narrow tube into carbonic acid and aniline. It contains $C_{14}H_6NO_3,HO$. By treatment with nitrous acid, anthranilic acid is converted into salicylic acid $C_{14}H_6NO_3,HO+NO_3=C_{14}H_5O_5,HO+HO+$

According to M. Cahours, pure indigo can also be converted into salicylic acid by fusion with hydrate of potassa; a particular temperature is required, somewhat above 570° (298°C), and the operation is by no means always successful.

LICHENS.

Litmus is used by the dyer as a red colouring matter; the chemist employs it in the blue state as a test for the presence of acid, by which it is instantly reddened.

In preparing test-papers for chemical use with infusion of litmus, good writing or drawing-paper, free from alum and other acid salts, should be chosen. Those sheets which after drying exhibit red spots or patches, may be reddened completely by a little dilute acetic acid, and used, with still greater advantage than turmeric-paper, to discover the presence of free alkali, which restores the blue colour.

Many lichens, when exposed in a moistened state to the action of ammonia, yield purple or blue colouring principles, which, like indigo, do not pre-exist in the plant itself. Thus, the *Roccella tinctoria*, the *Variolaria orcina*, the *Lecanora tartarea*, &c., when ground to paste with water, mixed with putrid urine or solution of carbonate of ammonia, and left for some time freely exposed to the air, furnish the *archil*, *litmus*, and *cudbear* of commerce, very similar substances, differing chiefly in the details of the preparation. From these the colouring matter is easily extracted by water or very dilute solution of ammonia.

The lichens have been extensively examined by Schunk, Stenhouse, and several other chemists. The whole subject has been lately revised by Dr. Strecker, whose formulæ have been adopted in the following succinct account:—

Erythric acid.—The lichen *Roccella tinctoria*, from which the finest kind of archil is prepared, is boiled with milk of lime, the filtered solution is precipitated by hydrochloric acid, and the precipitate dried and dissolved in warm, not boiling, alcohol, from which on cooling crystals of erythric acid are deposited. This is a very feeble acid, colourless, inodorous, difficultly soluble in cold and even in boiling water, readily soluble in ether. Its solution, when mixed with chloride of lime, assumes a blood-red colour. Boiled with water for some time, erythric acid absorbs 2 eq. and yields picro-erythrin, a crystallizable, bitter principle, and a new acid presently to be described, which is termed by some chemists *lecanoric*, by others *orsellinic* acid. If the ebullition be continued, the orsellinic acid undergoes a farther change, being converted into a crystalline substance, *orcin*, of which mention will shortly be made.

The composition of these various substances is expressed by the following formulæ:—

Erythric acid	$C_{20}H_{11}O_{10}$
Orsellinic acid	$C_{16}H_8O_8$
Picro-erythrin	$C_{24}H_{16}O_{14}$
Orcin	$C_{14}H_8O_4$

And the successive changes which occur by ebullition are represented by the following equation:—

$$\underbrace{2C_{20}H_{11}O_{10}+2HO}_{\text{Erythric acid.}} = \underbrace{C_{16}H_8O_8}_{\text{Orsellinic acid.}} + \underbrace{C_{24}H_{16}O_{14}}_{\text{Picro-erythrin.}}$$

$$\underbrace{C_{16}H_8O_8}_{\text{Orsellinic acid.}} = \underbrace{C_{14}H_8O_4}_{\text{Orcin.}} + 2CO_2$$

Alphaorsellic acid is obtained from the South American variety of *Roccella tinctoria*. The preparation and the properties of this substance are perfectly analogous to those of erythric acid. Alphaorsellic acid contains $C_{32}H_{14}O_{14}$; by boiling with baryta-water it likewise furnishes orsellinic acid.

$$\underbrace{C_{32}H_{14}O_{14}+2HO}_{\text{Alphaorsellic acid.}} = \underbrace{2C_{16}H_8O_8}_{\text{Orsellinic acid.}}$$

If the ebullition be continued too long, a great portion of the orsellinic acid is converted into orcin.

Orsellinic acid, formerly frequently called lecanoric acid, whether prepared from erythric or alphaorsellic acid, forms crystals which are far more soluble in water than either of the acids from which it has been prepared. Its taste is somewhat bitter. Boiled with water, it yields, as has been stated, orcin; under the influence of air and ammonia, it assumes a beautiful purple colour.

If the lichens, instead of being treated with milk of lime, be exhausted with boiling alcohol, the erythric and alphaorsellic acids are likewise decomposed; but instead of orsellinic acid, the ether of this substance, $C_4H_5O, C_{16}H_7O_7$, is formed. This ether was formerly described under the name *pseudo-erythrin* until Mr. Schunk pointed out the true nature of the substance. Orsellinate of ethyl may be likewise produced by boiling pure orsellinic acid with alcohol. It crystallizes in colourless lustrous plates, which are readily soluble in boiling water, alcohol, and ether.

Betaorsellic acid is found in *Roccella tinctoria* grown at the Cape; it is obtained like erythric and alphaorsellic acid, which it resembles in properties. Betaorsellic acid contains $C_{34}H_{16}O_{15}$; by boiling with water, it yields likewise orsellinic acid, together with hair-like crystals of a silvery lustre, a substance called *roccellinin*, which has the composition $C_{18}H_8O_7$.

$$\underbrace{C_{34}H_{16}H_{15}}_{\text{Betaorsellic acid.}} = \underbrace{C_{16}H_8O_8}_{\text{Orsellinic acid.}} + \underbrace{C_{18}H_8O_7}_{\text{Roccellinin.}}$$

The decomposition of betaorsellic acid is obviously analogous to that of erythric acid, the roccellinin representing the picro-erythrin.

Evernic acid is extracted by milk of lime from *Evernia prunastri*, which was formerly believed to contain orsellinic acid. Evernic acid is very difficultly soluble *even in boiling* water; it assumes a yellow colour with chlo-

ride of lime. When boiled with the alkalis, it yields another crystalline acid, everninic acid, differing from the preceding by its free solubility in boiling water. The composition of evernic acid is represented by the formula $C_{34}H_{16}O_{14}$, that of everninic acid by $C_{18}H_{10}O_{8}$. Evernic acid, when boiled for a considerable time with baryta, yields orcin: everninic acid does not give a trace of this substance; it is therefore probable that evernic acid, under the influence of alkalis, yields in addition to everninic acid likewise orsellinic acid, from which the orcin is derived, and that this decomposition is represented by the equation:—

$$\underbrace{C_{34}H_{16}O_{14}}_{\text{Evernic acid.}}+2HO \quad = \quad \underbrace{C_{16}H_{8}O_{8}}_{\text{Orsellinic acid.}} \quad + \quad \underbrace{C_{18}H_{10}O_{8}}_{\text{Everninic acid.}}$$

PARELLIC ACID.—*Lecanora parella* contains an acid probably analogous to erythric, alphaorsellic, betaorsellic, and evernic acids, the composition of which is, however, still unknown. By boiling with baryta it yields orsellinic acid and *parellic acid*, $C_{18}H_{6}O_{8}$.

ORCIN is the general product of decompositions of the acids previously described under the influence of heat or alkaline earths.

Orcin is best prepared by boiling lecanoric or orsellinic acid, pure or impure, with baryta-water, precipitating the excess of baryta by carbonic acid, and evaporating the filtered liquid to a small bulk. It forms, when pure, large, square prisms, which have a slightly yellowish tint, an intensely sweet taste, and a high degree of solubility both in water and alcohol. When heated, orcin loses water and melts to a syrupy liquid which distils unchanged. The crystals of orcin contain $C_{14}H_{8}O_{4}.2HO$.

ORCEIN.—When ammonia is added to a solution of orcin, and the whole exposed to the air, the liquid assumes a dark red or purple tint, by absorption of oxygen: a slight excess of acetic acid then causes the precipitation of a deep red powder, not very soluble in water, but freely dissolving in ammonia and fixed alkalis, with a purple or violet colour. This is an azotized substance, formed from the elements of the ammonia and the orcin, called *orcein*; it probably constitutes the chief ingredient of the red dye-stuff of the commercial articles before mentioned. The composition of orcein is less certain than that of orcin; it probably contains $C_{14}H_{7}NO_{6}$, when its formation from orcin, under the joint influence of oxygen and ammonia, would be represented by the equation:—

$$\underbrace{C_{14}H_{8}O_{4}.2HO}_{\text{Orcin.}}+6O+NH_{3} \quad = \quad \underbrace{C_{14}H_{7}NO_{6}}_{\text{Orcein.}}+6HO$$

Other substances are occasionally present in lichens; thus, the *Usnea barbata* and several other lichens contain *usnic acid*, a substance crystallizing from alcohol in fine yellowish-white needles with metallic lustre, having the formula $C_{34}H_{18}O_{14}$. It gives no orcin by distillation, but a substance similar to it, which probably contains $C_{38}H_{18}O_{6}$, and has been designated by the name of *betaorcin*. Its formation, which is attended by an evolution of carbonic acid, is represented by the equation:—

$$\underbrace{C_{38}H_{18}O_{14}}_{\text{Usnic acid.}} \quad = \quad \underbrace{C_{34}H_{18}O_{6}}_{\text{Betaorcin.}}+4CO_{2}$$

The *Parmelia parietina* furnishes another new substance, *chrysophanic acid*, crystallizing in fine golden-yellow needles and containing $C_{10}H_{4}O_{3}$. It is a very stable substance, and may be sublimed without much decomposition.

RED AND YELLOW DYES.

OCHINEAL.—This is a little insect, the *Coccus cacti*, which lives on several cies of *cactus*, which are found in warm climates, and cultivated for the pose, as in Central America. The dried body of the insect yields to water alcohol a magnificent red colouring matter, precipitable by alumina and le of tin; *carmine* is a preparation of this kind. In cochineal the colour- matter is associated with several inorganic salts, especially phosphates nitrogenetted substances. Mr. Warren De La Rue, who has published ery elaborate investigation of cochineal,[1] has separated the pure colouring tter, which he calls *carminic acid*, by the following process. The aqueous oction of the insect is precipitated by the acetate of lead, and the impure minate of lead washed and decomposed by hydrosulphuric acid; the ouring matter thus separated is submitted again to the same treatment. olution of carminic acid is thus obtained, which is evaporated to dryness, dissolved in absolute alcohol, and digested with crude carminate of lead, ereby a small quantity of phosphoric acid is separated, and lastly mixed h ether, which separates a trace of a nitrogenetted substance. The idue now obtained on evaporation is pure carminic acid. It is a purple- wn mass, yielding a fine red powder, soluble in water and alcohol in all portions, slightly soluble in ether. It is soluble without decomposition concentrated sulphuric acid, but readily attacked by chlorine, bromine, d iodine, which change its colour to yellow. It resists a temperature of 6°·8 (136°C), but is charred when heated more strongly. Carminic acid a feeble acid. The composition of the substance, dried at 248° (120°C), represented by $C_{28}H_{14}O_{16}$, which formula was corroborated by the analysis a copper-compound, $CuO,C_{28}H_{14}O_{16}$.

By the action of nitric acid upon carminic acid, together with oxalic acid, plendid nitrogenetted acid, crystallizing in yellow rhombic plates, is ob- ned. This substance, to which the name *nitrococcusic acid* was given, is asic; it contains $C_{16}H_{3}N_{3}O_{16},2HO$. It is soluble in cold, and more so in ling water, readily soluble in alcohol and ether. Nitrococcusic acid is lently derived from a non-nitrogenous compound in which part of the rogen is replaced by the elements of hyponitric acid. Like the sub- ces of this class, it explodes when heated.

n the mother-liquor, from which the carminic acid has been separated, Warren De La Rue discovered a white, crystalline, nitrogenetted sub- ce, for which he established the formula $C_{18}H_{11}NO_{6}$. This substance is tical with *tyrosine*, which will be mentioned in the section on Animal mistry.

[ADDER.—The root of the *Rubia tinctorum*, cultivated in southern France, Levant, &c., is the most permanent and valuable of the red dye-stuffs. Addition to several yellow colouring matters, which are of little impor- e for the purposes of the dyer, madder contains two red pigments which called *alizarin* and *purpurin*. These substances have been the subject of extensive researches by Debus, Higgins, and especially by Schunk. The st papers on madder have been published by Wolff and Strecker, whose nulæ are quoted in the following abstract.

LIZARIN.—The aqueous decoction of madder is precipitated by sulphuric l, and the precipitate washed and boiled with sesquichloride of aluminum, ch dissolves the red pigments; an insoluble brownish residue remaining ind. The solution, when mixed with hydrochloric acid, yields a precipi- consisting chiefly of alizarin, however, still contaminated with purpurin. impure alizarin thus obtained may be farther purified by again throwing

[1] Mem. of the Chem. Soc. vol. iii. p. 454.

down the alcoholic solution with hydrate of alumina, and boiling the preci-pitate with a concentrated solution of soda, which leaves a pure compound of alumina and alizarin behind. From this the alizarin is separated by hydrochloric acid, and re-crystallized from alcohol. Pure alizarin crystal-lizes in splendid red prisms, which may be sublimed. It is but slightly solu-ble in water and in alcohol, but dissolves in concentrated sulphuric acid with a deep red colour. On addition of water, the colouring matter is re-precipi-tated unchanged. It is also soluble in alkaline liquids, to which it imparts a magnificent purple colour. It is insoluble in cold solution of alum. Ali-zarin is the chief colouring matter of madder; it contains $C_{20}H_6O_6+4HO$, and is a feeble acid; but a few definite compounds with mineral oxides have been prepared, among which a lime-compound, $C_{20}H_6O_6,2CaO+3HO$, may be quoted. The action of nitric acid upon alizarin gives rise to the formation of oxalic acid and phthalic acid, a substance which will again be men-tioned among the products of decomposition of naphthalin.

$$\underbrace{C_{20}H_6O_6}_{\text{Alizarin.}}+2HO+8O=2(C_2O_3,HO)+\underbrace{C_{16}H_6O_8}_{\text{Phthalic acid.}}$$

PURPURIN.—Madder is allowed to ferment and then boiled with a strong solution of alum. The solution, when mixed with sulphuric acid, yields a red precipitate, which is purified by re-crystallization from alcohol. Purpurin thus obtained crystallizes in red needles, which contain $C_{18}H_6O_6+2HO$, i.e. 2 eq. of carbon less than alizarin. When treated with nitric acid, purpurin, like alizarin, furnishes oxalic and phthalic acids. Purpurin likewise con-tributes to the tinctorial properties of madder, but less so than alizarin. Together with alizarin and purpurin, several other substances occur in madder, among which may be noticed an orange pigment, *rubiacin*, convertible by oxidizing agents into a peculiar acid, *rubiacic acid*, a yellow pigment, *xanthin*, a bitter principle, *rubian*, *sugar*, pectic acid, and several *resins*, &c.

Garancin is a colouring material, which is produced by the action of sul-phuric acid upon madder. This substance possesses a higher tinctorial power than madder itself.

The beautiful *Turkey red* of cotton cloth is a madder-colour: it is given by a very complicated process, the theory of which is not perfectly elucidated. An abstract of it will be found in Prof. Graham's "Elements of Chemistry."

SAFFLOWER.—This substance contains a yellow and a red colouring matter, the latter being insoluble in water, but soluble in alkaline liquids. The saf-flower may be exhausted with water acidulated with acetic acid, and the solution mixed with acetate of lead, and filtered from the dark-coloured impure precipitate. The lead-compound of the yellow pigment may then be thrown down by addition of ammonia, and decomposed by sulphuric acid. In its purest form the yellow matter forms a deep yellow, uncrystallizable, and very soluble substance, very prone to oxidation. In its lead-compound it has probably the composition $C_{24}H_{12}O_{13}$.

The red matter or *carthamin* is obtained from the residual safflower by a dilute solution of carbonate of soda; pieces of cotton wool are immersed in the liquid, and acetic acid gradually added. The dried cotton is then digested in a fresh quantity of the alkaline solution, and the liquid supersaturated with citric acid, which throws down the carthamin in carmine-red flocks. It forms, when pure and dry, an amorphous, brilliant, green powder, nearly insoluble in water, but soluble in alcohol with splendid purple colour. It contains $C_{14}H_8O_7$.

Brazil-wood and *logwood* give red and purple infusions, which are largely used in dyeing; the colouring principle of logwood is termed hæmatoxylin

l has been obtained in crystals. This substance contains $C_{40}H_7O_{15}+8HO$. ids brighten these colours, and alkalis render them purple or blue.

Among yellow dyes, *quercitron-bark*, *fustic-wood*, and *saffron* may be men- ned, and also *turmeric;* these all give yellow infusions to water, and furnish ore or less permanent colours.

Purree or *Indian yellow*, a body of unknown origin, used in water-colour inting, according to the researches of Stenhouse and Erdmann, is a com- und of magnesia with a substance termed *purreic* or *euxanthic acid.* The tter, when pure, crystallizes in nearly colourless needles, sparingly soluble cold water, and of sweetish bitter taste. It forms yellow compounds with e alkalis and earths, and is decomposed by heat with production of a utral crystalline sublimate, *purrenone* or *euxanthone.* Purreic acid contains $H_{18}O_{21}$, purrenone $C_{13}H_4O_4$. By the action of chlorine, bromine, and nitric id, a series of substitution-products are formed.

Certain of the products of the action of nitric acid upon *aloes* resemble ry much some of the derivatives of indigo, without, however, it seems, ing identical with them. Powdered aloes, heated for a considerable time th excess of moderately strong nitric acid, yields a deep red solution, which posits on cooling a yellow crystalline mass. This, purified by suitable ans, constitutes *chrysammic acid;* it crystallizes in golden-yellow scales, ich have a bitter taste, and are but sparingly soluble in water. Its potassa- lt has a carmine-red tint, and exhibits a green metallic lustre, like that of rexide. The formula of chrysammic acid is not perfectly established. It probably $C_{14}HN_2O_{11},HO$. Like picric acid, it yields with chloride of lime, oropicrin. The mother-liquor from which the chrysammic acid has been osited contains a second acid, the *chrysolepic*, which also forms golden- low, sparingly soluble, scaly crystals. The potassa-salt forms small, low prisms, of little solubility. It explodes by heat. Chrysolepic acid tains $C_{12}H_2N_3O_{13},HO$; it is isomeric and possibly identical with picric acid. o these may be added the *styphnic acid* recently described by MM. ttger and Will, produced by the action of nitric acid of sp. gr. 1·2 upon *fœtida* and several other gum-resins and extracts. Purree, when treated a excess of nitric acid, likewise yields styphnic acid. It crystallizes, en pure, in slender, yellowish-white prisms, sparingly soluble in water, ily dissolved in alcohol and ether. It has a purely astringent taste, stains the skin yellow. By gentle heat it melts, and on cooling becomes stalline; suddenly and strongly heated, it burns like gunpowder. It also nishes chloropicrin. The salts of this substance mostly crystallize in nge-yellow needles, and explode with great violence by heat. Styphnic l contains $C_{12}H_2N_3O_{15},HO$, i. e., picric acid+2 eq. of oxygen. It may be wed as a nitro-substitute of the same acid, $C_{12}H_5O_3,HO$, which, by the in- luction of chlorine in the place of hydrogen, furnishes chloroniceic acid (page 463).

Hypothetical niceic acid........................	$C_{12}H_5,O_3,HO$
Chloroniceic acid..........	$C_{12}(H_4Cl)O_3,HO$
Trinitroniceic acid	$C_{12}H_2(NO_4)3O_3,HO$.

SECTION VII.

OILS AND FATS.

THE oils and fats form an interesting and very natural group of su which have been studied with great success The vegetable and an agree so closely in every respect, that it will be convenient to dis under one head.

Oily bodies are divided into *volatile* and *fixed:* the former are ca being distilled without decomposition, the latter are not. When di spread upon paper, they all produce a greasy stain; in the case o tile oil, this stain disappears when the paper is warmed, which neve with a fixed fatty substance. All these bodies have an attraction, less energetic, for oxygen: this in some cases reaches such a heig occasion spontaneous inflammation, as in the instance of large mass ton or flax moistened with rape or linseed oil. The effect of this a of oxygen leads to a farther classification of the fixed oils into d non-drying oils, or those which become hard and resinous by expos and those which thicken slightly, become sour and rancid, but neve To the first class belong the oils used in painting, as linseed, rape seed, and walnut; and to the second, olive and palm-oils, and all the fats of animal origin. The parts of plants which contain the larges ties of oil are, in general, the seeds. Olive-oil is, however, obtained fruit itself. The leaves of many plants are varnished on their uppe with a covering of waxy fat. Among the natural orders, that of the is conspicuous for the number of oil-bearing species.

The fixed oils in general have but feeble odour, and scarcely an whenever a sapid oil or fat is met with, it is invariably found to cont volatile oily principle, as in the case of common butter. They are a ble in water, and but slightly soluble in alcohol, with the exception o oil; in ether and in the essential oils, on the other hand, they di large quantity.

The consistence of these substances varies from that of the thinn oil to that of solid, compact suet: and this difference proceeds from able proportions in which the proximate solid and fluid fatty prin associated in the natural product. All these bodies may, in fact, mechanical means, or by the application of a low temperature, be s into two, or sometimes three, different substances, which dissolve t with each other, in all proportions. Thus, olive oil exposed to a 40° (4°·5C) deposits a large quantity of crystalline solid fat, whic separated by filtration and pressure: this is termed *margarin*, from aspect. That portion of the oil which retains its fluidity at this, o inferior degree of cold, has received the name *olein* or *elain*. Agai animal fat may, by pressure between folds of blotting-paper, be m harder, more brittle, and more difficult of fusion. The paper bec pregnated with a permanently fluid oil, or olein, while the solid par to consist of a mixture of two solid fats, one resembling the margari

, and the other having a much higher melting-point, and other properties ich distinguish it from that substance; it is called *stearin*.

Phese remarks apply to all ordinary oils and fats: it is, however, by no ans proved that the olein and margarin of all vegetable and animal oils e identical; it is very possible that there may be essential differences nong them, more especially in the case of the first-named substance.

Fixed fatty bodies, in contact with alkaline solutions at a high tempera- re, undergo the remarkable change termed *saponification*. When stearin, argarin, or olein, are boiled with a strong solution of caustic potassa or da, they gradually combine with the alkali, and form a homogeneous, scid, transparent mass, or *soap*, freely soluble in warm water, although in- luble in saline solutions. If the soap so produced be afterwards decom- osed by the addition of an acid, the fat which separates is found completely anged in character; it has acquired a strong acid reaction when applied a melted state to test-paper, and it has become soluble with the greatest cility in warm alcohol; it is in fact a new substance, a true *acid*, capable forming salts, and a compound ether, and has been generated out of the ements of the neutral fat under the influence of the base. Stearin, when us treated, yields *stearic acid*, margarin gives *margaric acid*, olein gives *ic acid*, and common animal fat, which is a mixture of the three neutral dies, affords by saponification by an alkali and subsequent decomposition the soap, a mixture of the three fatty acids in question. These bodies e not, however, the only products of saponification; the change is always companied by the formation of a very peculiar sweet substance, called *cerin*, which remains in the mother-liquor from which the acidified fat has en separated. The process of saponification itself proceeds with perfect ility in a close vessel; no gas is disengaged; the neutral fat, of whatso- er kind, is simply resolved into an alkaline salt of the fatty acid, or soap, d into glycerin.[1]

STEARIN AND STEARIC ACID. — Pure animal stearin is most easily obtained mixing pure mutton-fat, melted in a glass flask, with several times its ight of ether, and suffering the whole to cool. Stearin crystallizes out, ile margarin and olein remain in solution. The soft pasty mass may then transferred to a cloth, strongly pressed, and the solid portion still farther rified by re-crystallization from ether. It is a white friable substance, in- luble in water, and nearly so in cold alcohol; boiling spirit takes up a all quantity. Boiling ether dissolves it with great ease, but when cold tains only $\frac{1}{225}$ of its weight. The melting-point of pure stearin, which is e of its most important physical characters, may be placed at about 130° 4°·5C).

When stearin is saponified, it yields, as already stated, glycerin and stearic id. The latter crystallizes from hot alcohol in milk-white needles, which e inodorous, tasteless, and quite insoluble in water. It dissolves in its n weight of cold alcohol, and in all proportions at a boiling heat; it is ewise soluble in ether. Alkaline carbonates are decomposed by stearic id. Exposed to heat, it fuses, and at a higher temperature, if air be ex- uded, volatilizes unchanged. The melting-point of stearic acid is about 8° (70°C).

MARGARIN AND MARGARIC ACID. — The ethereal mother-liquor from which earin has separated in the process just described yields on evaporation a ft-solid mixture of margarin and olein with a little stearin. By compres-

[1] We are indebted to M. Chevreul for the first series of scientific researches on the fixed s and fats, and on the theory of saponification. These admirable investigations are detailed the early volumes of the "Annales de Chimie et de Physique," and were afterwards pub- hed in a separate form in 1823, under the title of "*Recherches chimiques sur les Corps gras Origine animale*."

sion between folds of blotting-paper, and re-solution in ether, it is rendered tolerably pure. In this state margarin very much resembles stearin; it is, however, more fusible, melting at 116° (46°·6C), and very much more soluble in cold ether. By saponification it yields glycerin and margaric acid. The properties of this last-named substance resemble in the closest manner those of stearic acid; it is different in composition, however, more soluble in cold spirit, and has a lower melting-point, viz., 140° (60°C) or thereabouts. Its salts also resemble those of stearic acid.

A more or less impure mixture of stearic and margaric acids is now very extensively used as a substitute for wax and spermaceti in the manufacture of candles. It is prepared by saponifying tallow by lime, decomposing the insoluble salt so formed by boiling with dilute sulphuric acid, and then pressing out the fluid or oily portion from the acidified fat.

The solid part of olive-oil is said to be a definite compound of true margarin and olein, inasmuch as its melting-point, 68° (20°C), is constant; it gives by saponification a mixture of margaric and oleic acids.

Olein and oleic acid.—It is doubtful whether a perfectly pure olein has yet been obtained; the separation of the last portions of margarin, with which it is always naturally associated, is a task of extreme difficulty. Any fluid oil, animal or vegetable, which has been carefully decolorized, and filtered at a temperature approaching the freezing-point of water, may be taken as a representative of the substance. Oleic acid much resembles olein in physical characters, being colourless and lighter than water, but it has usually a distinct acid reaction, a sharp taste, and is miscible with alcohol in all proportions. When submitted to the action of nitric acid, it yields almost the whole series of acids, of which formic, acetic, propionic, butyric, &c., are members, and which has been mentioned in a previous section of this work (see page 395).

When stearic or margaric acid, or ordinary animal fats, are exposed to destructive distillation, they yield margaric acid, a fatty body incapable of saponification, termed *margarone*, a liquid carbide of hydrogen, and various permanent gases. The neutral fats furnish besides an extremely pungent and even poisonous, volatile principle, called *acrolein*, described farther on.

In the manufacture of ordinary soaps both potassa and soda are used; the former yielding *soft*, and the latter *hard* soaps. Animal and vegetable fats are employed indifferently, and sometimes resin is added.

Composition of the preceding Substances.—The following are the formulæ at present assigned to the fatty acids in question: they are chiefly founded on investigations made at Giessen.

Stearic acid	$C_{68}H_{66}O_5.2HO$
Margaric acid	$C_{68}H_{66}O_6.2HO$.

Margaric is thus seen to differ from stearic acid in containing 1 eq. of oxygen more, and stearic acid can actually be converted into margaric by the action of oxidizing agents. Stearic acid is bibasic, and in its crystallized state contains 2 eq. of water. Margaric acid, as represented by the above formula, is likewise bibasic, but many chemists consider it as a monobasic acid $C_{34}H_{33}O_3,HO$: its bibasic nature being, in fact, by no means so well established as that of stearic acid. The subject requires farther examination, especially since an opinion has lately been expressed, that stearic and margaric acids are isomeric modifications of the same acid.[1]

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[1] According to Huntz, margaric acid is a mixture of stearic and palmitic acids, and that one part of stearic acid mixed with 9-10 parts of palmitic acid (melting at 144°; 62°·2C), produced a compound fusing at 140° (60°C), and possessing all the properties and ultimate composition of margaric acid. Moreover, when margaric acid obtained from mutton-fat was acted on by acetate of baryta, the first precipitate gave an acid melting at 135°·5 (57°C), and which

Oleic acid from almond-oil, butter, and beef-suet, gave results agreeing pretty well, and leading to the formula $C_{36}H_{33}O_3,HO$, the oleic acid of goose-fat, and olive-oil, having the same composition. Former researches had led to different results which are explained by the extreme proneness to oxidation of the substance itself. The oleic acid obtained from linseed-oil appears to differ from the preceding substance; its analysis having led to the formula $C_{46}H_{38}O_5,HO$. (?)

Margarone probably contains $C_{33}H_{33}O$, or margaric acid *minus* 1 eq. of carbonic acid.

The composition of stearin, margarin, and oleine is most safely deduced from a comparison of that of the acids to which they give rise, and of glycerin.

Margaric, stearic, and oleic acids have many properties in common; their salts much resemble each other, those of the alkalis being soluble in pure water when warm, but not in saline solution. A large quantity of cold water added to an alkaline margarate or stearate occasions the separation of a crystalline, insoluble acid salt. The margarates, stearates, and oleates of *lime*, *baryta*, and the oxides of the metals proper are insoluble in water. They are easily obtained by double decomposition, and in some few cases by direct action on the neutral fat. A solution of soap in alcohol is sometimes used as a test for the presence and quantity of lime, &c., in waters under examination (see page 241).

GLYCERIN.—This substance is very readily obtained by heating together olive or other suitable oil, protoxide of lead, and water, as in the manufacture of common *lead-plaster;* an insoluble soap of lead is formed, while the glycerin remains in the aqueous liquid. The latter is treated with sulphuretted hydrogen, digested with animal charcoal, filtered, and evaporated *in vacuo* at the temperature of the air. In a pure state, glycerin forms a nearly colourless and very viscid liquid, of sp. gr. 1·27, which cannot be made to crystallize. It has an intensely sweet taste, and mixes with water in all proportions; its solution does not undergo the alcoholic fermentation, but when mixed with yeast and kept in a warm place, it is gradually converted into propionic acid (see page 377). Glycerin has neither basic nor acid properties. Exposed to heat, it volatilizes in part, darkens, and becomes destroyed, one of its products of destruction being a substance possessing a most powerfully penetrating odour, which is called acrolein (see page 345). Nitric acid converts it into oxalic acid.

Glycerin is composed of $C_6H_8O_6$.

Glycerin combines with the elements of sulphuric acid, forming a compound acid, the *sulphoglyceric*, $C_6H_7O_5,2SO_3,HO$, which gives soluble salts with lime, baryta, and protoxide of lead.[1]

PALM AND COCOA OILS.—These substances, which at the common temperature of the air have a soft-solid or buttery consistence, are now largely consumed in this country. *Palm-oil* is the produce of the *Elais guianensis*, and comes chiefly from the coast of Africa. It has, when fresh, a deep orange-red tint, and a very agreeable odour; the colouring matter, the nature of

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fied without crystallizing; the other one, after repeated crystallization, melted at 142°·7 (61°·5 C), crystallized in needles, and exhibited the properties of palmitic acid. —R. B.

[1] Glycerin has been combined with acids. To effect this, the acid is mixed with the glycerin, and a current of hydrochloric acid passed through the mixture for several hours. This is set aside for periods, varying from a few days to several weeks. The hydrochloric acid is saturated by carbonate of soda, and then washed repeatedly.

These compounds are oleaginous, nearly or quite insoluble in water, do not unite with carbonated, but are slowly decomposed by caustic alkali, the glycerin separating unaltered.

Acetate of glycerin (acetine) has the appearance of a limpid, colourless oil, of a taste, at first, sweet, then sharp, the odour of acetic ether, and is volatile, without decomposition.

Valerate of glycerin (valerene) resembles phocenine, with which it should be identical.

Benzoate of glycerin (benzoicine) has an aromatic and peppery taste.—R. B.

which is unknown, is easily destroyed by exposure to light, especially at a high temperature, and also by oxidizing agents. The oil melts at 80° (26°·6 C). By cautious pressure it may be separated into a fluid olein and a solid substance, *palmitin*, which, when purified by crystallization from hot ether, is perfectly white, fusible at 118° (47°·8C), soluble to a small extent only in boiling alcohol, and convertible by saponification into *palmitic acid*. The latter resembles in the closest manner margaric acid, and has the same melting-point; it differs in composition, however, containing $H_{32}C_{31}O_3,HO$. By keeping, palm-oil seems to suffer a change similar to that produced by saponification; in this state it is found to contain traces of glycerin, and a considerable quantity of oleic acid, together with a solid fatty acid, first supposed to be margaric, which is probably palmitic acid. The oil becomes harder and rancid, and its melting-point is raised at the same time. *Cocoa-oil*, extracted from the kernel of the common cocoa-nut, is white, and has a far less agreeable smell than the preceding. It contains olein and a solid fat, often used as a substitute for tallow in making candles, which by saponification gives a crystallizable fatty acid, *cocinic acid*, having the usual properties of these bodies, and melting at 95° (35°·5C). It is composed of $C_{26}H_{25}O_3,HO$. Both this and palmitic acid are monobasic.

The solid vegetable fat from the *Myristica moschata* contains a volatile oil, a fluid olein, and a solid, crystallisable, fatty principle; this, when saponified, which occurs with difficulty, yields *myristic acid*. This substance has been examined by Dr. Playfair; it melts at 120° (48° 8C), and contains $C_{28}H_{27}O_3$, HO. It is monobasic.

Cacao-butter, extracted from the crushed beans by boiling with water, yields by saponification a fatty acid, identical, according to Dr. Stenhouse, with the stearic acid from animal fat.

Elaidin and elaidic acid. — When olive-oil is mixed with a small quantity of nitrous acid, nitric acid containing that substance, or solution of nitrate of mercury made in the cold, it becomes after a few hours a yellowish, soft-solid mass, which, pressed and treated with alcohol, furnishes a peculiar white, crystalline, fatty substance, termed *elaidin*. It resembles a neutral fat in properties, melts at 90° (32°·2C), dissolves with difficulty in boiling alcohol, easily in ether, and is resolved by saponification into glycerin and *elaidic acid*, which much resembles margaric acid. Oleic acid is directly convertible by nitrous acid into elaidic acid. It is not every kind of oil which furnishes elaidin; the drying oils, as those of linseed, poppy-seed, walnuts, &c., refuse to solidify; almonds, olive, and castor-oils possess the property in a high degree.

Elaidic acid appears to have the same composition as oleic acid, or $C_{36}H_{33}O_3,HO$.

Suberic, succinic, and sebacic acids. —*Suberic acid* has long been known as a product of the oxidation of *cork* by nitric acid (see page 345); *succinic acid* is obtained by the dilution of *amber*, a fossil resin. Recently both have been produced by the long-continued action of nitric acid upon stearic and margaric acids. Suberic acid is a white, crystalline powder, sparingly soluble in cold water, fusible and volatile by heat; it contains $C_{16}H_{12}O_6,2HO$. Succinic acid forms regular, colourless crystals, soluble in 5 parts of cold, and in half that quantity of boiling water; it is also fusible and volatile without decomposition, and contains $C_8H_4O_6,2HO$. The remarkable production of this substance from malic acid by a process of fermentation has been already mentioned (see page 415). *Sebacic acid* is a constant product of the destructive distillation of oleic acid, olein, and all fatty substances containing those bodies; it is extricated by boiling the distilled matter with water; it has also been lately formed by the action of potassa on castor-oil (see page 488). It forms small pearly crystals resembling those of benzoic

acid. It has a faint acid taste, is but little soluble in cold water, melts when heated, and sublimes unchanged. Sebacic acid is composed of $C_{10}H_8O_3,HO$ or $C_{20}H_{16}O_6,2HO$.

BUTTER; VOLATILE ACIDS OF BUTTER.—Common butter chiefly consists of a solid crystallizable, and easily fusible fat, a fluid oily substance, and a yellow colouring matter, besides mechanical impurities, as casein. The oily part appears to be a mixture of olein and a peculiar odoriferous fatty principle, *butyrin*, not yet isolated, which by saponification yields four distinct volatile acids, the *butyric*, the *caproic*, the *caprylic*, and the *capric*: these are most easily obtained by saponifying butter with potassa or soda, adding an excess of sulphuric acid, and distilling. The acid watery liquid obtained may then be saturated with an alkali, evaporated to a small bulk, and then distilled with excess of sulphuric or phosphoric acid in a retort. The mixed acids are separated by taking advantage of the unequal solubility of their baryta-salts; the less soluble salts of the mixture, amounting to about $\frac{1}{20}$ of the whole mass, contain capric and caprylic acids; the larger and more soluble portion, the caproic and butyric acids.

BUTYRIC ACID, when pure, is a thin colourless liquid, of pungent rancid odour and sour taste. It is miscible in all proportions with water and alcohol. Its density is 0·963, and it boils and distils unchanged at 327° (164°C). It is attacked by chlorine, with production of oxalic acid and of a chlorinetted compound not examined. Butyric acid contains $C_8H_7O_3,HO$.

CAPROIC ACID forms a colourless liquid, of sp. gr. 0·922, boiling at 388°·4 (198°C); it has a feeble odour, somewhat resembling that of acetic acid, and is much less soluble in water than butyric acid. It contains $C_{12}H_{11}O_3,HO$. The artificial formation of this acid from cyanide of amyl has been already noticed (see page 390). Caproic acid has been lately submitted to the action of the galvanic current. Messrs. Brazier and Gossleth have proved that it is analogous to that of valeric acid, and that the principal product is the hydrocarbon amyl $C_{10}H_{11}$ previously obtained by Dr. Frankland by the action of zinc upon iodide of amyl (see page 390).

CAPRYLIC ACID is chiefly remarkable for exhaling a powerful and disgusting odour of perspiration. It contains $C_{16}H_{15}O_3,HO$. This acid has been lately obtained by a very interesting reaction, namely, by the oxidation of the new caprylic alcohol discovered by M. Bouis among the products of decomposition of castor oil (see page 488).

CAPRIC ACID much resembles the caproic; it has a mixed odour of acetic acid and the smell of the goat, and is very sparingly soluble in water. Its formula is $C_{20}H_{19}O_3,HO$.

The simple relation existing between the formulæ of the volatile acids of butter, which are all members of the series of fatty acids, has been already pointed out (see page 395).

These acids exist ready formed in rancid butter and in cheese, associated with valeric acid. They are produced in small quantity by the saponification of most animal and some vegetable fats, and are generated, as has been mentioned already (see page 482), together with other products, by the action of nitric acid upon oleic acid. Butyric acid has been observed also as a product of the spontaneous decomposition of fibrin, and pre-exists in the leguminous fruit known as St. John's bread.

Whale and seal oil yield by saponification a volatile acid greatly resembling the preceding, called *phocenic* or *delphinic acid;* it was formerly believed to be a peculiar acid, but it is according to recent experiments nothing but valeric acid.

Butyric acid has acquired a certain degree of importance from the curious discovery of M. Pelouze, that sugar, under particular circumstances, is susceptible of becoming converted into that substance. A tolerably strong

solution of common sugar mixed with a small quantity of casein and some chalk, and exposed for some time to a temperature of 95° (35°C), yields, by a species of fermentation, in which the casein is the active *ferment*, a large amount of butyrate of lime; carbonic acid and hydrogen gases are extricated during the whole period. This change may be thus expressed—

$$\underbrace{C_{24}H_{28}O_{28}}_{\text{Grape-sugar.}} = 4HO + 8H + 8CO_2 + \underbrace{2(C_8H_7O_3,HO)}_{\text{Butyric acid.}}$$

The mixture directed for lactic acid answers well (see page 350); lactate of lime is first formed in large quantity, and afterwards gradually dissolved and converted into butyrate, which may be decomposed by sulphuric acid and distilled. This is an exceedingly interesting case of the half-artificial formation of an animal product.

WAX.—*Common bees-wax*, freed from its yellow colouring matter by bleaching, may be separated by boiling alcohol into two different proximate principles, *cerin* and *myricin*. The first is a white crystalline substance, soluble in about 16 parts of boiling spirit, and melting at 144° (62°·2C); it is the more abundant of the two. It is easily saponified by a solution of caustic potassa. According to Brodie's valuable experiments it consists chiefly of cerotic acid $C_{54}H_{53}O_3,HO$, which belongs to the series of fatty acids (see page 395). The same body in a very interesting form of combination exists in *Chinese wax*, which, according to Brodie, is a compound ether containing cerotic acid combined with the ether of cerotylic alcohol $C_{54}H_{55}O,HO$. It may be viewed as cerotate of oxide of cerotyl $C_{54}H_{55}O$, $C_{54}H_{53}O_3$ corresponding to the acetic ether of the wine-alcohol-series. When heated with potassa it undergoes the changes peculiar to compound ethers, yielding on the one hand cerotate of potassa, and on the other hand cerotylic alcohol. Myricin is very much less soluble in alcohol, and rather more fusible. It is saponified with difficulty by a dilute solution of caustic potassa, palmitic acid $C_{32}H_{31}O_3,HO$ (see page 484), combines with the potassa, and a substance $C_{60}H_{61}O,HO$, belonging to the series of alcohols, is set free, which has been termed melissic alcohol. Hence myricin is likewise a compound ether, namely, palmitate of oxide of melissyl $C_{92}H_{92}O_4 = C_{60}H_{66}O,C_{32}H_{33}O_3$.

SPERMACETI.—The soft-solid matter found in very large quantity in a remarkable cavity in the head of the spermacetic whale, when submitted to pressure, yields, as is well known, a most valuable fluid oil, and a crystalline, brownish substance, which, when purified, becomes the beautiful snow-white article of commerce, spermaceti. This substance appears, by the most recent experiments, to be a neutral fatty body of the constitution of compound ethers, and not, as formerly supposed, a mixture of several proximate principles. It melts at 120° (48°·8C), and when cooled under favourable circumstances, forms distinct crystals. Boiling alcohol dissolves it in small quantity, and ether in much larger proportion. Spermaceti is saponified with great difficulty: two products are obtained, a substance $C_{32}H_{34}O_2$ belonging to the series of alcohols (see page 394), to which the name *cetylic* (*ethalic*) *alcohol* has been given, and *cetylic* (*ethalic*) *acid* $C_{32}H_{32}O_4$; the first is a crystallizable fat, whose melting-point is nearly the same as that of spermaceti itself, but its solubility in alcohol is much greater; it is also readily sublimed without decomposition. Cetylic acid stands to cetylic alcohol in the same relation as acetic acid to ordinary alcohol, and may be actually procured from the latter by oxidation; it resembles in many respects margaric acid. By oxidation by nitric acid, spermaceti yields a large quantity of succinic acid.

Spermaceti is composed of $C_{64}H_{66}O_4 = C_{32}H_{33}O,C_{32}H_{31}O_3$; it is cetylate of

oxide of cetyl, and represents in the cetyl-series the acetic ether of the common alcohol-series.[1]

Cholesterin.—This substance is found in small quantity in various parts of the animal system, as in the bile, in the brain and nerves, and in the blood; it forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling, the cholesterin crystallizes in brilliant, colourless plates. It has the characters of a fat, is insoluble in water, tasteless and inodorous; it is freely soluble in boiling water, and also in ether. It altogether resists saponification. Cholesterin melts at 278° (136°C), and contains probably $C_{26}H_{22}O$.

Cantharidin, the active principle of the Spanish fly, may be here mentioned. It is a colourless, crystallizable, fatty body, extracted by ether or alcohol from the insect; it is insoluble in water and dilute acids, and volatile when strongly heated. The vapour attacks the eyes in a very painful manner. Cantharidin contains $C_{10}H_6O_4$.

Acrolein.—When a neutral fat is subjected to destructive distillation, it furnishes, as already mentioned, among other products, an excessively volatile acrid substance, which attacks the eyes and the mucous membrane of the nose most distressingly. As the neutral fats alone yield this body, and the fatty acids never, it is known to arise from the elements of the glycerin; and glycerin itself under certain circumstances may be made to produce acrolein abundantly. It is best prepared by distilling glycerin with bisulphate of potassa; both the preparation and purification are attended with great difficulties.

Pure acrolein is a thin, colourless, highly volatile liquid, lighter than water, and boiling at 126° (52°·9C). Its vapour is irritating beyond description. It is sparingly soluble in water, freely in alcohol and ether. According to M. Redtenbacher it contains $C_6H_4O_2$.

When exposed for some time to the air, or when mixed with oxide of silver, acrolein oxidizes with avidity, and passes into *acrylic acid*, which resembles in very many particulars acetic and propionic acids; it contains $C_6H_3O_3,HO$. Acrolein by keeping undergoes partial decomposition, yielding a white, flocculent, indifferent body, *disacryle;* the same substance is sometimes produced together with acrylic acid by exposure to the air. In contact with alkalis, acrolein suffers violent decomposition, producing, like aldehyde, a resinous body.

The action of sulphuric acid upon olive-oil has been studied by M. Frémy. When the oil is slowly and cautiously mixed with half its volume of concentrated sulphuric acid, all rise of temperature being avoided, a homogeneous liquid is obtained, which, when mixed with a little water, separates into two layers, the undermost consisting of sulpho-glyceric and free-sulphuric acid, and the upper and syrupy portion of two compound acids, the *sulphomargaric* and *sulpholeic*. These latter dissolve in a large quantity of water, but after some time undergo decomposition into sulphuric acid and several new fatty acids, to which the names *metamargaric*, *hydromargaric*, *hydromargaritic*, *metoleic*, and *hydroleic* were given. The first three are derived from the ele-

[1] According to the investigations of Heintz, the composition of spermaceti is of a very complex character, consisting of a series of acids differing in constitution by C_2H_2 combined with ethal, viz.:—

Margethal	= margarate of oxide of cetyl	$C_{34}H_{33}O_3,C_{32}H_{33}O$
Palmethal	= palmitate	$C_{32}H_{31}O_3,C_{32}H_{33}O$
Cetethal	= cetate	$C_{30}H_{29}O_3,C_{32}H_{33}O$
Myristethal	= myristate	$C_{28}H_{27}O_3,C_{32}H_{33}O$
Cocethal	= *cocinate*	$C_{26}H_{25}O_3,C_{32}H_{33}O$.—R. B.

ments of the sulphomargaric acid: they are solid and crystallizable, and much resemble ordinary margaric acid, differing slightly from that substance and from each other in their melting-points, degree of solubility in alcohol, &c. The metoleic and hydroleic acids are fluid, and are derived from the sulpholeic acid of the mixture. They yield carbonic acid and liquid hydrocarbons by destructive distillation. The composition of these fatty acids is yet uncertain, but in all probability they only differ from margaric and oleic acids by the elements of water. The action of sulphuric acid upon the oil is thus somewhat similar to the effect of saponification, the neutral fat being resolved into margaric and oleic acids and glycerin, the whole of which then combine with the elements of sulphuric acid to form compounds belonging to the large group of substances of which sulphovinic acid is the typical member.

The sulphuric saponification of fatty bodies is now carried out on a very large scale for producing cheaper varieties of "*stearin candles.*" For this purpose, inferior fatty bodies, such as palm-oil, are mixed with 5 or 6 per cent. of concentrated sulphuric acid, and exposed to a temperature of 350° (177°C) produced by overheated steam. After cooling, the black mass thus obtained crystallizes to a tolerably solid fat, which is washed once or twice with water, and then submitted to distillation by the aid of steam, heated to about 560° (293°·5C). The product of the distillation, which is beautifully white, may be at once used for making candles; frequently, however, it undergoes the processes of *cold* and *hot* pressing, whereby a much more solid fat is obtained.

Castor oil, which differs in some respects from the ordinary vegetable oils, yields, by oxidation with nitric acid, a peculiar product, namely, a volatile fatty acid to which the term *œnanthylic* has been applied. It forms a colourless, oily liquid of aromatic odour and burning taste, and slightly soluble in water. It refuses to solidify at a very low temperature, and cannot be distilled alone without some decomposition, although its vapour passes over readily with that of water. This body has distinct acid properties, forms a series of salts and an ether, and contains $C_{14}H_{13}O_3,HO$. Under the influence of the galvanic current it undergoes a decomposition similar to that of valeric acid, according to Messrs. Brazier and Gossleth, the principal product being, together with a hydrocarbon containing equal equivalents of carbon and hydrogen, an oily substance $C_{12}H_{13}$, boiling at 395°·6 (202°C), to which the name *caproyl* has been given, and which may be viewed as the radical of the alcohol of caproic acid $C_{12}H_{13}O,HO$, still to be discovered.

Castor-oil has lately become the source of a new alcohol in the hands of M. Bouis. According to his researches, there is present in castor-oil a peculiar oleic acid, *ricinoleic acid*, which contains $C_{36}H_{33}O_5,HO$, i. e., 2 eq. of oxygen more than common oleic acid. If this acid, or more conveniently castor-oil itself, be heated with solid hydrate of potassa, an oily liquid distils over, boiling at 356° (180°C), which is the alcohol of caprylic acid. It contains $C_{16}H_{17}O,HO$, and is readily converted into caprylic acid (see page 485), by treatment with oxidizing agents. The residue in the retort contains sebacate of potassa. This transformation is represented by the following equation:—

$$\underbrace{C_{36}H_{33}O_5,HO}_{\text{Ricinoleic acid.}} + 2(KO,HO) = \underbrace{2KO,C_{20}H_{16}O_6}_{\text{Sebacate of potassa.}} + \underbrace{C_{16}H_{17}O,HO}_{\text{Caprylic alcohol.}} + 2H$$

VOLATILE OILS.

The volatile oils of the vegetable kingdom are exceedingly numerous; they are secreted by plants, and confer upon their flowers, fruits, leaves, and

mod their peculiar odours. These substances are mostly procured by dis-lling the plant, or part of the plant, with water; their points of ebullition ways lie above that of water; nevertheless, at 212° (100°C) the oils emit apour of very considerable tension, which is carried over mechanically, and ondensed with the steam. The milky, or turbid liquid obtained, when left rest, separates into oil and water. Sometimes the oil is heavier than the ater, and sinks to the bottom; sometimes the reverse happens.

The volatile oils, when pure, are colourless; they very frequently, how-ver, have a yellow, and in rarer cases, a green colour, from the presence f impurity. The odour of these substances is usually powerful, and their aste pungent and burning. They resist saponification completely, but when xposed to the air frequently become altered by slow absorption of oxygen, nd assume the character of resins. They mix in all proportions with fat ils, and dissolve freely both in ether and alcohol; from the latter solvent hey are precipitated by the addition of water. As already mentioned, the olatile oils communicate a greasy stain to paper, which disappears by warm-ng; by this character any adulteration with fixed oils can be at once de-ected. A solid, crystalline matter, corresponding to the margarine of the ommon oils, frequently separates from these bodies; it bears the general ame of *stearoptene*, and differs probably in almost every case.

The essential oils may be conveniently divided into three classes; viz., hose consisting of carbon and hydrogen only; those consisting of carbon, ydrogen, and oxygen; and those containing in addition sulphur and nitrogen.

Oils composed of Carbon and Hydrogen.

OIL, OF ESSENCE OF TURPENTIN.—This substance may be taken as the type r representative of the class; it is obtained by distilling with water the soft r semi-fluid balsam called in commerce *crude turpentine*, which exudes from arious pines and firs, or flows from wounds made for the purpose in the wood. The solid product left after distillation is common resin. Oil of tur-pentin, when farther purified by rectification, is a thin, colourless liquid, of powerful and well-known odour: its density in the liquid state is 0·865, and that of its vapour 4·764; it boils at 312° (155°·5C). In water it dis-solves to a small extent, and in strong alcohol and ether much more freely; with fixed oils it mixes in all proportions. Strong sulphuric acid chars and blackens this substance; concentrated nitric acid and chlorine attack it with such violence that inflammation sometimes ensues.

Oil of turpentin is composed of C_5H_4 or $C_{20}H_{16}$.

With hydrochloric acid the oil forms a curious compound, which has been called *artificial camphor* from its resemblance in odour and appearance to that substance. It is prepared by passing dry hydrochloric acid gas into the pure oil, cooled by a freezing mixture. After some time, a white, crys-talline substance separates, which may be strained from the supernatant brown and highly acid liquid, and purified by alcohol, in which it dissolves very freely. This substance is neutral to test-paper, does not affect nitrate of silver, and sublimes without much decomposition; it contains $C_{20}H_{17}$,Cl, or perhaps $C_{20}H_{16}$,HCl. The dark mother-liquid contains a somewhat similar, but fluid compound. Different specimens of oil of turpentin yield very variable quantities of these substances, which may, perhaps, arise from the co-existence of *two* very similar and isomeric oils in the ordinary article. When these hydrochlorates are decomposed by distillation with lime, they yield liquid oily products differing in some particulars from the original oil of turpentin, but have the same composition as that substance. That from the solid has received the name of *camphylene*, and that from the liquid com-pound *terebylene*. The hypothetical and non-isolable modifications of the oil

supposed to exist in the solid camphor are termed respectively *camphene* and *terebene*.

Another isomeric compound, *colophene*, is produced by distilling oil of turpentin with concentrated sulphuric acid. It is a viscid, oily, colourless liquid, of high boiling-point, and exhibiting by reflected light a deep blue tint,—a phenomenon often remarked in bodies of this class.

Bromine and iodine also form compounds with oil of turpentin.

Oil of turpentin is very largely used in the arts, in painting, and as a solvent for resins in making varnishes.

Bottles in which rectified oil of turpentin, not purposely rendered anhydrous, has been preserved, are often studded in the interior with groups of beautiful, colourless, prismatic crystals, which form spontaneously. These have the composition of a hydrate of oil of turpentin. These crystals contain $C_{20}H_{16}H_6O_6$.

Oil of lemons is expressed from the rind of the fruit, or obtained by distillation with water. This oil differs very much from the last in odour, but closely resembles it in other respects. It has the same composition as oil of turpentin, and forms with hydrochloric acid two compounds; one solid and crystalline, the other fluid. The solid contains $C_{10}H_8HCl$.

The oils of *orange-peel*, *bergamot*, *pepper*, *cubebs*, *juniper*, *copaiva*, *elemi*, the *laurel-oil* of Guiana, the East Indian *grass-oil*, and the principal part of hop-oil, are hydrocarbons, isomeric with the oils of turpentin and lemons.

Essential Oils containing Oxygen.

The essential oils containing oxygen are very numerous, and in fact make up the great bulk of the bodies of this class employed in medicine and perfumery. They are seldom homogeneous, and in consequence do not often exhibit fixed boiling-points. Some of these oils have been made the subjects of much chemical research, but the majority yet require examination. Three of the most interesting, viz., those of bitter almonds, cinnamon, and the *Spiræa ulmaria* have been already described.

Oil of aniseed.—The oil distilled from the seeds of the *Pimpinella anisum* consists of two substances, one of which is a fluid oil, and the other a solid crystalline substance, so abundant as to cause the whole to solidify at a temperature of 50° (10°C). By pressure between folds of bibulous paper and crystallization from alcohol, the solid essence may be obtained pure. It forms colourless pearly plates, more fragrant in odour than the crude oil, which melt when gently heated, and distil at a high temperature. It contains $C_{20}H_{12}O_2$. This substance is attacked energetically by chlorine, bromine, and nitric acid; it combines with hydrochloric acid, but is unaffected by solution of caustic potassa. With bromine the solid essence yields a white inodorous crystallizable compound, *bromanisal*, containing $C_{20}(H_9Br_3)O_2$. The action of chlorine is more complex, several successive compounds being produced. With sulphuric acid two products are obtained, a compound acid analogous to sulphovinic acid, and a white, solid neutral substance, *anisoin*, isomeric with the essence.

The products of the action of nitric acid vary with the strength of the acid employed; the most important are *hydride of anisyl; anisic acid*, a substance very much resembling salicylic acid in properties, sparingly soluble in cold water, freely in alcohol and ether; *nitranisic acid*, a yellowish-white, crystalline sparingly-soluble powder; and *nitraniside*, a resinous body produced by fuming nitric acid.

The hydride of anisyl in a pure state is a yellowish oily liquid, having an aromatic odour of hay; it is heavier than water, and boils at 400° (254°·5C). Caustic potassa, concentrated and boiling, slowly decomposes it; with fused

e of potassa, it is instantly converted into anisic acid with disengage- f hydrogen; air and oxidizing bodies in general produce the same Ammonia forms with it a crystalline compound analogous to hydro- aide. Hydride of anisyl contains $C_{16}H_8O_4$.

iic acid contains $C_{16}H_7O_5,HO$, i. e., hydride of anisyl and 2 eq. of ı. When treated with an excess of lime or baryta, it suffers a decom- n, analogous to that of benzoic and salicylic acid, losing 2 eq. of car- acid, and being converted into an oxygenated oil, boiling at 302° !), to which the name *anisol* has been given.

$$\underbrace{C_{16}H_7O_5,HO}_{\text{Anisic acid.}}+2CaO=2(CaO,CO_2)+\underbrace{C_{14}H_8O_2}_{\text{Anisol.}}$$

anisic acid is the nitro-substitute of anisic acid; it contains $C_{16}(H_6$ $_5$,HO.

solid portion of the oils of bitter fennel and badian is identical with f oil of aniseed. The fluid component of the fennel-oil is isomeric il of turpentin.

conic acid, obtained by the action of nitric acid upon the oil of *Arte- racunculus*, is identical with anisic acid.

various substances belonging to this group are homologous to the ers of the salicyl-series, described in a former part of the Manual ige 404), as may be seen from the following comparison:—

ride of salicyl.........	C_{14}	H_6	O_4;	C_{16}	H_8	O_4	Hydride of anisyl.
ylic acid	C_{14}	H_6	O_6;	C_{16}	H_8	O_6	Anisic acid.
osalicylic (anilic) id	C_{14}	$\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}$	O_6;	C_{16}	$\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$	O_6	Nitranisic acid.
iol (hydrate of phe- l)	C_{12}	H_6	O_2;	C_{14}	H_8	O_2	Anisol.

OF CUMIN is a mixture of two bodies, separable in great measure by tion, *cymol*, a liquid hydrocarbon, containing $C_{20}H_{14}$, the most volatile ı of the oil, and *cuminol*, a colourless transparent oil, of powerful odour, changed in the air, and only to be distilled in a current of carbonic acid Cuminol contains $C_{20}H_{12}O_2$, and is consequently isomeric with the solid of aniseed. By oxidation, this substance, which is homologous to oil er almonds, yields *cumic acid*, a white, fatty, volatile substance, insolu- water, having but little odour, and crystallizing in prismatic tables. ains $C_{20}H_{11}O_3,HO$ (see homologues of benzoic acid, page 403).

OF CEDAR-WOOD, in like manner, contains two substances, a solid crys- compound, having the formula $C_{32}H_{26}O_2$, and a volatile liquid hydro- , *cedrene*, $C_{32}H_{24}$, which can also be obtained by distilling the solid ahydrous phosphoric acid.

OF GAULTHERIA PROCUMBENS.—This very remarkable substance is now in commerce under the name of *winter-green-oil;* it consists almost of a definite principle which distils unchanged at 435° (223°·8C), and is, according to the analysis of M. Cahours, $C_{16}H_8O_6$. When mixed with caustic potassa, it solidifies to a crystalline mass, which is a potassa- *ultherate* of potassa, and from which the oil may be separated again ged on the addition of an acid. When distilled, however, with a con- ed solution of caustic potassa, the oil of gaultheria is resolved into c acid and wood-spirit, thus exactly resembling in its behaviour the nd ethers which have been described in a previous section of the l (see page 352). This oil is, in fact, a veritable compound ether, *te of oxyde of methyl*, $C_2N_3O,C_{14}H_5O_5=C_{16}H_8O_6$, furnished by nature With ammonia the oil yields salicylamide, $C_{14}H_7NO_4=C_{14}H_5O_4,NH_2$, with anthranilic acid (see page 474), which is converted by fuming

nitric acid into the nitro-substitute, nitro-salicylamide (anilamide) $C_{14}(H_4NO_4.)O_4.NH_2$, crystallizing in yellowish-white needles. Gaultheria oil is isomeric with anisic acid (see page 491), and yields by distillation at a high temperature with anhydrous lime and baryta, *anisol* $C_{14}H_8O_2$, the same volatile oily liquid which is obtained from anisic acid by a similar process.

Oil of valerian.—The oil obtained by distilling valerian-root with water has usually a viscid consistence, a yellowish colour, and a powerful and disagreeable odour. It consists of at least three principles, namely, *valeric acid, borneene* (see camphor), a light volatile liquid hydrocarbon, much resembling and isomeric with oil of turpentin, and *valerol*, a neutral oily body, much less volatile than the preceding, of feeble odour, and convertible by oxidizing agents into valeric acid. It contains $C_{12}H_{10}O_2$. Borneene, under certain circumstances not well understood, assimilates the elements of water and yields the solid camphor of Borneo, or *borneol*.

Camphor.—Common camphor yields a good example of a concrete essential oil; it is obtained by distilling with water the wood of the *Laurus camphora*. When pure, it forms a solid, white, crystalline, and translucent mass, tough, and difficult to powder, and having a powerful and very familiar odour. It melts when gently heated, and boils, distilling unchanged at a high temperature. It slowly sublimes at the temperature of the air, and often forms beautiful crystals on the sides of bottles or jars containing it exposed to the light. Camphor is very sparingly soluble in water, but readily soluble in alcohol, ether, and strong acetic acid. It contains $C_{10}H_8O$, or $C_{20}H_{16}O_2$.

By the action of nitric acid aided by heat, camphor is gradually oxidized and dissolved with production of *camphoric acid;* this substance forms small colourless needles or plates, of acid and bitter taste, sparingly soluble in cold water, and containing $C_{10}H_7O_3.HO$. It melts when heated, and yields by distillation a colourless, crystalline, neutral substance, containing $C_{10}H_7O_3$, improperly termed anhydrous camphoric acid.

When camphorate of lime is submitted to distillation, it yields a volatile oil containing oxygen, in its formation and constitution similar to acetone (page 376) or benzophenone (page 398). This substance, *phorone*, contains C_9H_7O or $C_{18}H_{14}O_2$. By the action of anhydrous phosphoric acid it loses water and furnishes the hydrocarbon *cumol*, $C_{18}H_{12}$ (see page 403).

When camphor in vapour is passed over a mixture of hydrate of potassa and quicklime strongly heated in a tube, it is resolved without disengagement of gas into an acid body termed *campholic acid*, white, crystalline, and sparingly soluble in water, containing $C_{20}H_{17}O_3.HO$. By distillation with anhydrous phosphoric acid, this acid gives a volatile hydrocarbon, *campholene*. Camphor itself, by a similar mode of treatment, yields a colourless volatile liquid, $C_{20}H_{14}$, formerly called *camphogen*, but since found to be identical with the hydrocarbon, cymol, occurring in oil of cumin.

The camphor of Borneo, procured from the *Dryabalanops camphora*, contains $C_{20}H_{18}O_2$; it is accompanied by borneene, identical with that of the oil of valerian, and yields the same substance when distilled with anhydrous phosphoric acid. Nitric acid converts it into common camphor.

The oils of *peppermint, lavender, rosemary, orange-flowers, rose-petals*, and many others, belong to the class of oxygenated essential oils.

Essential Oils containing Sulphur.

In the preparation of the sulphuretted volatile oils, distillatory vessels of copper, tin, or lead must be avoided, as those metals are attacked by the sulphur. In other respects their manufacture offers no peculiarities.

Oil of mustard.—The most remarkable member of the class is the oil obtained by distillation from black mustard-seed. White mustard yields

hone. Both varieties give, by expression, a bland fat oil. The volatile oil does not pre-exist in the seed, but is formed in the same manner as bitter-almond-oil, by the joint action of water and a peculiar coagulable albuminous matter upon a substance yet inperfectly known, present in the grain, and termed *myronic acid.*

The distilled oil, when pure, is colourless; it has a most powerful, pungent and suffocating smell, and a density of 1·015. Applied to the skin, it produces almost instant vesication. It boils at 289° (145°·8C). Water dissolves it in small quantity, and alcohol and ether very freely. The oil itself, at a high temperature, dissolves both sulphur and phosphorus, and deposits them in a crystalline form on cooling. It is oxidized with violence by nitric acid, and by *aqua regia.* Alkalis decompose it by the aid of heat, with production of ammonia, an alkaline sulphide, and a sulphocyanide. The remarkable compound with ammonia, thiosinnamine, has been already described (see page 466.)

Mustard-oil gives by analysis $C_8H_5NS_2$.

The oil of horse-radish, and that obtained from the roots of the *Alliaria officinalis* by distillation with water, are identical with the oil of black mustard-seed.

Oil of garlic.—The crude oil procured by distilling the sliced bulbs with water is not a homogeneous product; by the action of metallic potassium, however, renewed until it is no longer tarnished, a small portion of oxygenetted oil which it contains may be decomposed and withdrawn, after which the sulphuretted compound may be obtained pure by re-distillation. In this state it forms a colourless liquid, lighter than water, of high refractive power, possessing in a high degree the peculiar odour of the plant, and capable of being distilled without decomposition. It contains C_6H_5S. Garlic-oil dissolved in alcohol, and mixed with solutions of platinum, silver, and mercury, gives rise to crystalline compounds having the characters of double salts, containing the elements of the oil with the sulphur replaced by oxygen or chlorine.

A curious and interesting relation exists between the oils of mustard and garlic: in both these substances, we may assume the existence of a radical C_6H_5, to which the name *allyl* has been given, when mustard-oil becomes the sulphocyanide, and garlic-oil the sulphide of allyl.

Mustard-oil $C_8H_5NS = C_6H_5C_2NS_2$.		Sulphocyanide of allyl.
Garlic-oil $C_6H_5S = C_6H_5S$.		Sulphide of allyl.

This relation has been experimentally established. By mixing the oil with hydrate of soda and quicklime, and exposing the whole in an hermetically-sealed tube to a temperature superior to that of boiling water, sulphocyanide of sodium is produced, together with an oily substance which is *oxide of allyl,* a substance chiefly known in combination, and which is the oxygenetted constituent of crude garlic-oil. Again, if mustard-oil be treated in a similar manner with sulphide of potassium, sulphocyanide of potassium and garlic-oil are formed. On the other hand, when the compound of garlic-oil and chloride of mercury is gently heated with sulphocyanide of potassium, mustard-oil, with all its characteristic properties, is called into existence.

The oils of *assafœtida,* and *onions,* contain sulphur, and consequently belong to the same series; they have not yet been thoroughly examined.

RESINS AND BALSAMS.

Common resin, or *colophony,* furnishes perhaps the best example of the class. The origin of this substance has been already described. It is a mixture of two distinct bodies, having acid properties; called pinic and sylvic

[illegible] from each other by their difference of solubility in cold and [illegible] alcohol, the former being by far the more soluble of the two. [illegible]ic acid crystallizes in small, colourless, rhombic prisms, inso[illegible] water, soluble in hot, strong alcohol, in volatile oils, and in ether. It [illegible] when heated, but cannot be distilled without decomposition. The properties of pinic acid are very similar. Both have the same composition, viz., $C_{20}H_{15}O_{2}$. A third resin-acid, also isomeric with the preceding, the *pimaric*, has been found in the turpentin of the *Pinus maritima* of Bordeaux.

Lac is a very valuable resin, much harder than colophony, and easily soluble in alcohol; three varieties are known in commerce, viz., *stick-lac*, *seed-lac*, and *shellac*. It is used in varnishes, and in the manufacture of hats, and very largely in the preparation of sealing-wax, of which it forms the chief ingredient. Crude lac contains a red dye which is partly soluble in water. Lac dissolves in considerable quantity in a hot solution of borax; Indian ink, rubbed up with this liquid, forms a most excellent *label-ink* for the laboratory, as it is unaffected by acid vapours, a[illegible]en once dry, becomes nearly insoluble in water.

Mastic, *Dammar-resin*, and *sandarac* [illegible]sins largely used by the varnish-maker. *Dragon's-blood* is a resin of a d[illegible] red colour. *Copal* is also a very valuable substance; it differs from the[illegible]r resins, in being with difficulty dissolved by alcohol and essential oils. [illegible] miscible, however, in the melted state with oils, and is thus made into [illegible]h. *Amber* appears to be a fossil resin; it is found accompanying brown-c[illegible]or lignite.

CAOUTCHOUC.—This curious, and now m[illegible]t useful substance, is the produce of several trees of tropical countries, whic[illegible] yield a milky juice, hardened by exposure to the air. In a pure stat[illegible] nearly white, the dark colour of commercial caoutchouc being due to [illegible]ots of smoke and other impurities. Its physical characters are [illegible]wn. It is softened, but not dissolved by boiling water; it is also insol[illegible]uble in alcohol. In pure ether, rectified native naphtha, and coal-oil, it dissolves, and is left unchanged on the evaporation of the solvent. Oil of turpentin also dissolves it, forming a viscid, adhesive mass, which dries very imperfectly. At a temperature a little above the boiling-point of water caoutchouc melts, but never afterwards returns to its former elastic state. Few chemical agents affect this substance; hence its great practical use, in chemical investigations, for connecting apparatus, &c. Analysis shows it to contain nothing but carbon and hydrogen.

By destructive distillation caoutchouc yields a large quantity of thin volatile oily liquid, of naphtha-like odour, to which the name *caoutchoucin* has been applied. This is probably a mixture of several hydrocarbons, scarcely to be separated from each other by distillation or otherwise. It dissolves caoutchouc with facility.

A substance much resembling caoutchouc in certain respects, and of similar origin, has lately been introduced under the name of *gutta percha*. It is capable of many useful applications in the laboratory.

Most of the resins, when exposed to destructive distillation, yield liquid, oily pyro-products, usually carbides of hydrogen, which have been studied with partial success. Great difficulties occur in these investigations; the task of separating from each other, and isolating bodies which scarcely differ but in their boiling-points, is exceedingly troublesome.

Balsams are also, as before hinted, natural mixtures of resins with volatile oils. These differ very greatly in consistence, some being quite fluid, others solid and brittle. By keeping, the softer kinds often become hard. Balsams may be conveniently divided into two classes, viz., those which, like common and *Venice turpentin*, *Canada balsam*, *copaiba balsam*, &c., are merely natural varnishes, or solutions of resins in volatile oils, and those which contain ben-

oic or cinnamic acid in addition, as *Peru* and *Tolu balsams*, and the solid resinous *benzoin* commonly called *gum-benzoin*.

Tolu-balsam, by distillation with water, yields three products; namely, *benzoic acid*, *cinnamein*, and *tolene*, a volatile colourless hydrocarbon, boiling at 338° (170°C), and containing $C_{10}H_8$. The balsam freed in this manner from essential oils, exposed to destructive distillation, yields in succession a viscous liquid which crystallizes in the receiver, and a thin liquid heavier than water; carbonic acid and carbonic oxide are largely evolved, and the retort is afterwards found to contain a residue of charcoal. The solid product is chiefly a mixture of benzoic and cinnamic acids; the volatile oil contains at least two substances differing in their boiling-points, and easily separated, namely, *toluol* (benzoene), which has been mentioned already as a derivative of toluylic acid (see page 403), and an oily liquid heavier than water, of high boiling-point, and having the composition and characters of benzoic ether.

Toluol is a thin, colourless liquid, insoluble in water, sparingly soluble in alcohol, more freely in ether; it has the odour of benzol; its sp. gr. is 0·870, and it boils at 226° (107°·5C). The density of its vapour is 3·26, and its formula $C_{14}H_8$. It combines with fuming sulphuric acid to the compound *sulphotuolic acid*: with nitric acid it yields two products, *nitrotoluol*, $C_{14}H_7NO_4$, and *binitrotoluol*, $C_{14}H_6N_2O_8$. The former is fluid, heavier than water, and bears a great resemblance in odour and other properties to nitrobenzol; the latter is a solid, fusible, crystallizable substance. The conversion of nitrotoluol into the organic base toluidine, has been already described (see page 462).

Liquid storax distilled with water, holding in solution a little carbonate of soda, yields a small and variable quantity of volatile oil, not homogeneous, but from which, by careful distillation, a liquid volatile hydrocarbon, termed *styrol*, can be extracted in a state of purity. It is thin and colourless, of powerful aromatic odour, refuses to solidify when cooled to 0° (—17°·8C), and boils at 293° (145°·C). Its sp. gr. is 0·924; it is nearly insoluble in water, but mixes freely with alcohol and ether. Styrol contains $C_{16}H_8$, and is consequently isomeric with benzol. This substance is also produced by the action of lime or baryta upon cinnamic acid (see page 408), whence it is more appropriately termed *cinnamol*.

When a portion of styrol is hermetically sealed in a glass tube, and then exposed for half an hour to a temperature approaching 400° (204°·5C) by means of an oil-bath, it undergoes a most remarkable change, becoming converted into a solid, transparent, glassy, fusible substance, called *metastyrol*, isomeric, as might be expected, with styrol itself. The same change is slowly produced by the influence of sunshine. A portion of metastyrol is always formed when styrol is distilled in a retort without water. Metastyrol is again convertible by distillation at a high temperature into liquid styrol.

Certain of the products of the distillation of dragon's-blood appear to be identical with these bodies.

SECTION VIII.

COMPONENTS OF THE ANIMAL BODY.

ALBUMINOUS PRINCIPLES. [illegible] e fluid portion of blood which has been some time drawn f[illegible] dy, and the white of eggs, contain this substance as [illegible] racteristic ingredient. In the purest form in which alb[illegible] btained it is insoluble, or nearly so, in water If clear s[illegible] hite of egg mixed with a little water and filtered, be e[illegible] y acetic acid, and then largely diluted with pure cold wat[illegible] cculent precipitate falls, which may be collected on a filter, [illegible] this state it is nearly colourless, inodorous, and tasteles[illegible] ith facility in water containing an exceedingly small quantity [illegible] kali, and gives a solution which has all the characters of the [illegible] l. When dried by gentle heat, it shrinks to a very small b[illegible] nes a translucent, horny mass, which softens in water, and e[illegible] posed to heat the usual ammoniacal products of animal ma[illegible] bulky coal, very difficult of combustion When white of egg is thinly spread upon a plate and exposed to evaporation in a warm place, it dries up to a pale yellow, brilliant, gum-like substance, destitute of all traces of crystalline structure. In this state it may be preserved unchanged for any length of time, the presence of water being in all cases necessary to putrefactive decomposition. The dried white of egg may also be exposed to a heat of 212° (100°C) without alteration of properties. When put into slightly warm water, it softens, and at length in great measure dissolves. When reduced to fine powder and washed upon a filter with cold water, common salt, sulphate, phosphate, and carbonate of soda are dissolved out, together with mere traces of organic matter, while a soft swollen mass remains upon the filter, which has all the characters of pure albumin obtained by precipitation. When dried and incinerated, this leaves nothing but a little phosphate of lime.

It thus appears likely that albumin is really an insoluble substance, and that its soluble state in the animal system is due to the presence of a little alkali.

When natural albumin is exposed to heat it solidifies, or *coagulates*. The temperature required for this purpose varies with the state of dilution. If the quantity of albumin be so great that the liquid has a slimy aspect, a heat of 145° or 150° (62°·5 or 65°·5C) suffices, and the whole becomes solid, white, and opaque; in a very dilute condition, boiling is required, and the albumin then separates in light, finely divided flocks. Thus changed by heat, albumin becomes quite insoluble in water: it dries up to a yellow, transparent, horny substance, which when macerated in water resumes its former whiteness and opacity. In dilute caustic alkali it dissolves with facility, and in this respect resembles the insoluble albumin just described; it differs, however, from the latter in not being soluble in a strong solution

e of potassa, which dissolves with great ease that substance. The mical change that can be traced in the act of coagulation is the loss and soluble salts, which are removed by the hot water.

tion of ordinary albumin gives precipitates with excess of sulphuric, oric, nitric, and *meta*-phosphoric acids; but neither with acetic nor ımon or tribasic phosphoric acid. These precipitates, which, though n water, are insoluble in an excess of dilute acid, are looked upon t compounds of albumin with the acids in question. Most of the salts, as those of copper, lead, mercury, &c., form insoluble com- with albumin, and give precipitates with its solution; hence the white of egg as an antidote in cases of poisoning with corrosive e. Alcohol, added in large quantity, precipitates albumin. Tannic infusion of galls, gives with it a copious precipitate. By these cha- he presence of albumin may be readily discovered, and its identi- effected; a *very* feebly alkaline liquid, if containing albumin, coagu- heat, becomes turbid on the addition of nitric acid, and previously ed by acetic acid, gives a precipitate with solution of corrosive e. It must be remembered, that a considerable quantity of alkali, minute quantities of the mineral acids, prevent coagulation by heat, addition of acetic acid, indispensable to the mercury-test, produces effect.

emical composition of albumin has been carefully studied; it con- 100 parts:—

Carbon	53·5
Hydrogen	7·0
Nitrogen	15·5
Oxygen	22·0
Phosphorus	0·4
Sulphur	1·6
	100·0

xistence of unoxidized sulphur in albumin is easily shown; a boiled kens a silver spoon from a trace of alkaline sulphide formed or sepa- ring the coagulation; and a solution of albumin in excess of caustic mixed with a little acetate of lead, gives on boiling a black preci- ntaining sulphide of lead.

N.—This substance is found in solution in the blood. It is procured ing the coagulum of blood in a cloth until all the soluble portions oved, or by agitating fresh blood with a bundle of twigs, when the taches itself to the latter, and is easily removed and cleansed by l washing with cold water. The only impurity then remaining is a antity of fat, which can be extracted by ether. In the fresh state rms long, white, elastic filaments; it is quite tasteless, and inso- both hot and cold water. By long-continued boiling it is partly d. When dried *in vacuo*, or at a gentle heat, it loses about 80 per water, and becomes translucent and horny; in this state it closely es coagulated albumin. Fresh fibrin wetted with concentrated acetic rms, after some hours, a transparent jelly, which slowly dissolves water; put into a very dilute caustic alkali, fibrin dissolves com- and the solution exhibits many of the characters of albumin. Phos- cid produces a similar effect. Boiled with strong hydrochloric acid ral hours, fibrin is converted into a mixture of *leucine* (see page 477) *sine* (see page 500).

brin of arterial and venous blood is not absolutely the same; when *us fibrin of human* blood is triturated in a mortar with 1½ times its ? *

weight of water and ⅛ of its weight of nitrate of potassa, and then left 24 hours or more at a temperature of 100°—120° (37·7—48 becomes gelatinous, slimy and eventually entirely liquid: in this it exhibits all the properties of a solution of albumin which has b [illegible] by acetic acid. It coagulates by heat, it is precipitated by corrosive sublimate, &c., and when largely diluted it deposits a substance, not to be distinguished from insoluble albumin.[1] With fibrin, on the contrary, no such liquefaction happens, and even the [illegible] fibrin, when long exposed to the air, or to oxygen gas, loses property in question.

In the soluble state, fibrin is in great measure unknown; when from the influence of life, it coagulates spontaneously after a certain giving rise to the production of the clot which appears in blood left and which consists of a kind of fine net-work of fibres, swollen w serum, and inclosing the little red colouring particles of the blood, to be described.

Mr. Mulder found dried fibrin, carefully freed from fat, to be com follows: —

Carbon	52·7
Hydrogen	6·9
Nitrogen	15·4
Oxygen	23·5
Phosphorus	0·3
Sulphur	1·2
	100·0

The ash, or incombustible portion of fibrin, varying from 0·7 to cent. consists chiefly of the phosphate of lime.

CASEIN. — This is the characteristic azotized component of milk, basis of the various preparations termed cheese; it is not known to any other secretion. Casein very closely resembles albumin in ma ticulars, and may even be occasionally confounded with it. Like th stance, it is insoluble in water when in a state of purity, and only the soluble condition in the presence of free alkali, of which, however small quantity suffices for the purpose. To prepare casein, fresh gently warmed with dilute sulphuric acid, the coagulum produced well with water, dissolved in a dilute solution of carbonate of soda, and p a warm situation to allow the fat or butter to separate from the liquid. The latter is then removed by a siphon, and re-precipitated phuric acid. These precipitations and re-solutions in dilute alkali are times repeated. Lastly, the insoluble casein is well washed with water, and treated with ether to remove the last traces of fat. In th it is a white curdy substance, not sensibly soluble in pure water or in but dissolved with great ease by water containing a little caustic o nated alkali. It is also soluble to a certain extent in dilute aci which it may be precipitated by cautious neutralization. The pre formed by an acid in a strong solution of casein contains acid in comb which, however, may be entirely removed by washing. In the moi casein reddens litmus-paper, and masks the reaction of an alkali bonate. When incinerated, it leaves about 0·3 per cent. of incom matter.

A solution of casein in very dilute alkali, as in milk, does not co on boiling. On evaporation the surface becomes covered by a skin,

[1] Liebig, Handwörterbuch der Chemie, i. 881.

— eventually dries up to a translucent mass. Acetic acid precipitates ..., which is a distinctive character between that substance and albumin. ...usion with hydrate of potassa casein yields valerianic and butyric ...besides other products.

...most striking property of casein is its coagulability by certain animal ...anes. This is well seen in the process of cheese-making, in the pre-...n of the *curd*. A piece of the stomach of the calf, with its mucous ...ane, is slightly washed, put into a large quantity of milk, and the ...slowly heated to about 122° (50°C). In a short time after this tem-...re has been attained, the milk is observed to separate into a solid, ...coagulum, or mass of curd, and into a yellowish, translucent liquid ...*whey*. The curd contains all the casein of the milk, much of the fat, ...uch of the inorganic matter; the whey retains the milk-sugar and the ... salts. It is just possible that this mysterious change may be really ... the formation of a little lactic acid from the milk-sugar, under the ... influence of a slowly decomposing membrane and the elevated tempe-...re, and that this acid may be sufficient in quantity to withdraw the ...i which holds the casein in solution, and thus occasion its precipitation ... insoluble state. The loss of weight the membrane itself suffers in this ...ation is very small; it has been found not to exceed $\frac{1}{1800}$ part.

...asein has been carefully analysed by Mulder; it contains in 100 parts—

Carbon	53·83
Hydrogen	7·15
Nitrogen	15·65
Oxygen, Sulphur	23·37
	100·00

...hen precipitated by acetic acid and washed with alcohol and ether it ...tains about 1 per cent. of sulphur. When not treated with acid it con-...s about 6 per cent. of phosphate of lime.

... comparison of the composition of these three bodies described is very ...arkable, as it shows that they are very closely related in composition. ... fibrin contains rather a larger quantity of oxygen than the albumin, and ... casein contains no phosphorus. As, however, it is very doubtful whether ...se substances have been obtained in an unmixed and pure state no for-...le can be given.

...ROTEIN.—Mulder observed that when albumin, fibrin, or casein was dis-...ved in a moderately strong solution of caustic alkali, and digested at 140° ...°C), or thereabouts, in an open vessel until the liquid ceased to blacken ...h a salt of lead, and then filtered, and mixed with a slight excess of ...tic acid, a copious, snow-white flocculent precipitate fell, and a faint odour ...sulphuretted hydrogen was evolved. The new substance he called pro-...n.[1] He stated that it was free from sulphur and phosphorus, and that it ... by the combination of different quantities of these elements with pro-...n, that albumin, fibrin, and casein, were produced, the protein pre-existing ...each of these substances. It is, however, now admitted, that neither by ... above-mentioned treatment, nor in any way, can a substance free from ...phur be obtained, and the protein must therefore be considered as one of ... first products of the decomposition of albumin, fibrin, and casein, by ...lerately strong caustic alkali.

...hen albumin, fibrin, or casein, are boiled in strong solution of potassa

[1] So called from πρωτεύω, *I take the first place*; in allusion to its alleged important relations ... *albuminous principles*.

as long as ammoniacal vapours are given off, the liquid then neutralised with sulphuric acid, evaporated to dryness, and the product exhausted by boiling alcohol, three compounds are dissolved out, viz., a soluble, brown extract-like substance, *erythroprotide;* a soluble straw-yellow substance, *protide*, and a curious crystallizable principle, *leucine*, which forms small colourless scales, destitute of taste and odour, soluble in water and alcohol, and in concentrated sulphuric acid without decomposition. When heated, it sublimes unchanged. Leucine contains $C_{12}H_{13}NO_4$, (see page 501).

Binoxide and Teroxide of Protein.—These names were given by Mulder to products of the long-continued action of boiling water upon fibrin in contact with air; they are said to be the chief ingredients also of the *buffy* coat of blood in a state of inflammation, being produced at the expense of the fibrin.[1] They cannot be obtained free from sulphur. *Binoxide of protein* is quite insoluble in water, but dissolves in dilute acids; when dry, it is [illegible] coloured. The soluble part of the fibrin-decoction contains *teroxide of protein*, which somewhat resembles, and has been confounded with, gelatin. It is freely soluble in boiling water, and in dilute alkalis. Coagulated albumin is slowly dissolved by boiling water, and said to be converted into this substance. The solution in cold water gives a precipitate with nitric acid which is re-dissolved on the application of heat, and re-precipitated when cold. A substance closely resembling this in its reactions and composition has been found in the urine of a patient suffering from *molleties ossium.*[2]

When chlorine gas is passed to saturation into a solution of ordinary albumin, or either fibrin or casein dissolved in ammonia, a white, flocculent, insoluble substance falls, which, when washed and dried, becomes a soft yellowish powder. This is supposed to be a compound of chlorous acid and protein; when digested with ammonia, it yields sal-ammoniac and teroxide of protein.

Gelatin and chondrin.—Animal membranes, skin, tendons, and even bones, dissolve in water at a high temperature more or less completely, but with very different degrees of facility, giving solutions which on cooling acquire a soft-solid, tremulous consistence. The substance so procured is termed *gelatin;* it does not pre-exist in the animal system, but is generated from the membranous tissue by the action of hot water. The jelly of calves' feet, and common size and glue, are familiar examples of gelatin in different conditions of purity. Isinglass, the dried swimming-bladder of the sturgeon, dissolves in water merely warm, and yields a beautifully pure gelatin. In this state it is white and opalescent, or translucent, quite insipid and inodorous, insoluble in cold water, but readily dissolving by a slight elevation of temperature. Cut into slices and exposed to a current of dry air, it shrinks prodigiously in volume, and becomes a transparent, glassy, brittle mass, which is soluble in warm water, but insoluble in alcohol and ether. Exposed to destructive distillation, it gives a large quantity of ammonia, inflammable gases, nauseous empyreumatic oil, and leaves a bulky charcoal containing nitrogen. In a dry state, gelatin may be kept indefinitely; in contact with water, it putrefies. Long-continued boiling gradually alters it, and the solution loses the power of forming a jelly on cooling. 1 part of dry gelatin or isinglass dissolved in 100 parts of water solidifies on cooling.

An aqueous solution of gelatin is precipitated by alcohol, which withdraws the water; corrosive sublimate in excess gives a white flocculent precipitate, and the same happens with solution of nitrate of the sub- and protoxide of mercury; neither alum, acetate, nor basic acetate of lead affect a solution of gelatin. With tannic acid or infusion of galls, gelatin gives a copious,

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[1] Mulder, Annalen der Chemie und Pharmacie, xlvii. 323.
[2] See Philosophical Trans. 1848.

itish, curdy precipitate, which coheres on stirring to an elastic mass, te insoluble in water, and incapable of putrefaction.

Chlorine passed into a solution of gelatin occasions a dense white precipie of *chlorite of gelatin*, which envelopes each gas-bubble, and ultimately ms a tough, elastic, pearly mass, somewhat resembling fibrin. Boiling th strong alkalis converts gelatin, with evolution of ammonia, into leucine, d a sweet crystallizable principle, *gelatin-sugar*, or *glycocoll*, or better, *ycocine* containing $C_4H_5NO_4$. This remarkable substance was first formed the action of cold concentrated sulphuric acid upon gelatin, and has ely been obtained by the action of acids upon hippuric acid, which is ereby resolved into benzoic acid and glycocine (see page 402). It forms lourless crystals, freely soluble in water, and unites to crystallizable comunds with a great number of bodies, acids, bases and salts. Glycocine, hen treated with nitrous acid, yields an acid homologous to lactic acid (see ge 402), to which the name of glycolic acid has been given.

$$\underbrace{C_4H_5NO_4}_{\text{Glycocine.}} + NO_3 = \underbrace{C_4H_4O_6}_{\text{Glycolic acid.}} + 2N + HO$$

This substance, which is but imperfectly studied, appears to be present likewise in the mother-liquor from which the fulminate of silver has been deposited. There exists a remarkable relation between glycocine, alanine, and leucine, two substances which have been previously described (pages 467 and 500). These three bodies are homologous, as will be seen from the following formulæ :—

Glycocine	$C_4H_5NO_4$
Alanine	$C_6H_7NO_4$
Leucine	$C_{12}H_{13}NO_4$.

The deportments of these three substances with nitrous acid is perfectly alike. Leucine, according to M. Strecker, yields a new acid $C_{12}H_{12}O_6$ homologous to glycolic and lactic acids, which has not yet been perfectly examined.

When a dilute solution of gelatin is distilled with a mixture of bichromate of potassa and sulphuric acid, it yields a number of extraordinary products, as acetic, valerianic, benzoic, and hydrocyanic acids, and two volatile oily principles termed *valeronitrile* and *valeracetonitrile*. The former is a thin colourless liquid, of aromatic odour, like that of hydride of salicyl; it is lighter than water, boils at 257° (125°C), and contains $C_{10}H_9N$. The latter much resembles the first, but boils at 158° (70°C), and contains $C_{26}H_{24}N_2O_6$. Alkalis convert valeronitrile into valerianic acid and ammonia, and valeracetonitrile into valerianic and acetic acids and ammonia. It is very probable that the latter compound is a mixture of acetonitrile and valeronitrile.

Dry gelatin, subjected to analysis, has been found to contain in 100 parts :—

Carbon	50·05
Hydrogen	6·47
Nitrogen	18·35
Oxygen	25·13
	100·00

From these numbers the formulæ $C_{13}H_{10}N_2O_5$, and $C_{52}H_{40}N_8O_{20}$, have been deduced.

The cartilage of the ribs and joints yields a gelatin differing in some respects from the preceding; it is called, by way of distinction, chondrin.

Acetate of lead and solution of alum precipitate this substance, which is not the case with common gelatin. To chondrin the formulæ [illegible] and $C_{48}H_{40}N_6O_{20}$ have been given.

If a solution of gelatin, albumin, fibrin, casein, or probably any [illegible] the more complex azotized animal principles, be mixed with solution of [illegible]phate of copper, and then a large excess of caustic potassa added, the greenish precipitate first formed is re-dissolved, and the liquid acquires a purple tint of indescribable magnificence and great intensity.

Gelatin is largely employed as an article of food, as in soups, &c.; but its value in this respect has been much overrated. In the useful arts, size and glue are consumed in great quantities. These are prepared from the clippings of hides, and other similar matters, inclosed in a net, and boiled with water in a large cauldron. The strained solution gelatinises on cooling, and constitutes *size*. Glue is the same substance in a state of desiccation, the size being cut into slices and placed upon nettings, freely exposed to a current of air. Gelatin is extracted from bones with much greater difficulty; the best method of proceeding is said to be to inclose the bones, previously crushed, in strong metallic cylinders, and admit high-pressure steam, which attacks and dissolves the animal matter much more easily than boiling water; or, to steep the bones in dilute hydrochloric acid, thereby removing the earthy phosphate, and then dissolve the soft and flexible residue by boiling.

There is an important economical application of gelatin, or rather of the material which produces it, which deserves notice, viz., to the clarifying of wines and beer from the finely divided and suspended matter which [illegible] renders these liquors muddy and unsightly. When isinglass is digested in very dilute cold acetic acid, as sour wine or beer, it softens, swells, and assumes the aspect of a very light transparent jelly, which, although quite insoluble in the cold, may be readily mixed with a large quantity of watery liquid. Such a preparation, technically called *finings*, is sometimes used by brewers and wine-merchants for the purpose before-mentioned; its action on the liquor with which it is mixed seems to be purely mechanical, the gelatinous matter slowly subsiding to the bottom of the cask, and carrying with it the insoluble substance to which the turbidity was due.

Kreatin and kreatinine. — Kreatin was first observed by Chevreul, and has lately been studied very carefully by Professor Liebig, who obtained it from the soup of boiled meat; it is best prepared from the juice of raw flesh by the following process: — A large quantity of lean flesh is cut up into shreds, exhausted by successive portions of cold water, strained and pressed. The liquid, which has an acid reaction, is heated to coagulate albumin and colouring matter of blood, and passed through a cloth. It is then mixed with pure baryta-water as long as a precipitate appears, filtered from the deposit of phosphates, and evaporated in a water-bath to a syrupy state. After standing some days in a warm situation, the kreatin is gradually deposited in crystals, which are easily purified by re-solution in water and digestion with a little animal charcoal.

When pure, kreatin forms colourless, brilliant, prismatic crystals, which become dull by loss of water at 212° (100°C). They dissolve readily in boiling water, sparingly in cold, and are but little soluble in alcohol. The aqueous solution has a weak bitter taste, followed by a somewhat acrid sensation. In an impure state the solution readily putrifies. Kreatin is a neutral body, not combining either with acids or alkalis. In the crystallized state it contains $C_8H_9N_3O_4,2HO$.

By the action of strong acids, kreatin is converted into *kreatinine*, a powerful organic base, with separation of the elements of water. The new substance forms colourless prismatic crystals, and is much more soluble in water

tin; it has a strong alkaline reaction, forms with acids crystalli-, and contains $C_8H_7N_3O_2$.

ine pre-exists to a small extent in the juice of flesh, together with l and other bodies yet imperfectly examined. It is also found in n with kreatin in urine.

reatin is long boiled with solution of caustic baryta, it is gradually nto urea, subsequently decomposed into carbonic acid and ammo- new organic body of basic properties, *sarcosine.* The latter, when ns colourless transparent plates, extremely soluble in water, soluble in alcohol, and insoluble in ether. When gently heated and sublime without residue. Sarcosine forms with sulphuric acid zable salt, and contains $C_6H_7NO_4$, being isomeric with lactamide, nd urethane.

ther-liquid from flesh from which the kreatine has been deposited among other things, a new acid, the *inosinic,* the aqueous solution refuses to crystallize. It has a strong acid reaction, and is preci- a white amorphous condition by alcohol. It probably contains $_{0}$, HO.[1] Recently, moreover, a kind of sugar, which however does nt, has been found in the juice of flesh. It was discovered by who calls it *inosite,* and gives the composition $C_{12}H_{12}O_{12}+4HO$ ance crystallizes in beautiful crystals.

ITION OF THE BLOOD; RESPIRATION.—The blood is the general cir- uid of the animal body, the source of all nutriment and growth, eneral material from which all the secretions, however much they r in properties and composition, are derived. Food or nourish- without can only be made available by being first converted into ; serves also the scarcely less important office of removing and off principles from the body which are hurtful, or no longer re-

ertebrated animals the blood has a red colour, and probably in all mperature above that of the medium in which the creature lives. mmalia this is very apparent, and in the birds still more so. The e blood is directly connected with the degree of activity of the y process. In man the temperature of the blood seldom varies n 98° (36°·6C), when in a state of health, even under great vicissi- climate; in birds it is sometimes as high as 109° (42°·8C). To highest classes of the animal kingdom, the mammifers and the observations about to be made are intended especially to apply.

y creature of this description two kinds of blood are met with, er very considerably in their appearance, viz., that contained in le of the heart and in the arteries generally, and that contained it side of the heart and in the veins; the former, or *arterial* blood, ght red colour, the latter, the *venous* blood, is blackish purple. he conversion of the dark into the florid blood may be traced to s place during its exposure to the air in the lungs, and the oppo- e, to what takes place in the capillaries of the general vascular the minute tubes or passages, distributed in countless numbers t the whole body, which connect the extremities of the arteries When compared together, little difference of properties or com- an be found in the two kinds of blood; the fibrin varies a little, venous blood being, as already mentioned, soluble in a solution of potassa, which is not the case with arterial fibrin. It is very sides, to absorb oxygen, and to become in all probability partly o the substance called binoxide of protein, which no doubt exists

[1] Liebig, Chemistry of Food.

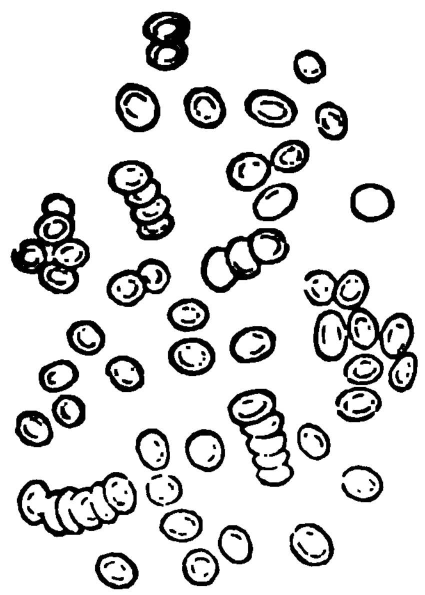
in the fibrin of arterial blood. The only other notable point of difference is in the gaseous matter the blood holds in solution, carbonic acid predominating in the venous, and free oxygen in the arterial variety.

In its ordinary state the blood has a slimy feel, a density varying from 1·053 to 1·057, and a decidedly alkaline reaction; it has a saline and disagreeable taste, and, when quite recent, a peculiar odour or *halitus*, which almost immediately disappears. An odour may, however, afterwards be developed by an addition of sulphuric acid, which is by some considered characteristic of the animal from which the blood was obtained.

The coagulation of blood in repose has been already noticed, and its cause traced to the spontaneous solidification of the fibrin: the effect is best seen when the blood is received into a shallow vessel, and left to itself some time. No evolution of gas or absorption of oxygen takes place in this process. By strong agitation coagulation may be prevented; the fibrin in this case separates in cohering filaments.

To the naked eye the blood appears a homogeneous fluid, but it is not so in reality. When examined by a good microscope, it is seen to consist of a transparent and nearly colourless liquid, in which float about a countless multitude of little round red bodies, to which the colour is due; these are the *blood-discs* or *blood-corpuscles* of microscopic observers. Fig. 174. They are accompanied by colourless globules, fewer and larger, the *white corpuscles of the blood*.

Fig. 174.



The *blood-discs* are found to present different appearances in the blood of different animals: in the mammifers they look like round red or yellowish discs, thin when compared with their diameter, being flattened or depressed on opposite sides. In birds, lizards, frogs, and fish, the corpuscles are elliptical. In magnitude, they seem to be pretty constant in all the members of a species, but differ with the genus and order. In man they are very small, varying from $\frac{1}{5000}$ to $\frac{1}{3000}$ of an inch in breadth, while in the frog the long diameter of the ellipse measures at least four times as much. The corpuscles consist of an envelope containing a fluid in which the red colouring-matter of the blood is dissolved.

The coagulation of blood effects a kind of natural proximate analysis: the clear, pale serum, or fluid part, is an alkaline solution of albumin, containing various soluble salts; the clot is a mechanical mixture of fibrin and blood globules, swollen and distended with serum, of which it absorbs a large but variable quantity.

When the coagulum of blood is placed upon bibulous paper, and drained as much as possible from the fluid portion, and then put into water, the envelope, which consists of globulin, dissolves and sets free the colouring matter, forming a magnificent crimson solution, which has many of the characters of a dye-stuff. It contains albumin and globulin, and coagulates by heat and by the addition of alcohol; this albumin and globulin cannot be separated, and attempts to isolate the *hematosin* or red pigment have consequently failed. From its extreme susceptibility of change, it is not known in a state of purity. The above watery solution, exposed with extensive surface in a warm place, dries up to a dark red, brittle mass, which is again soluble in water. After coagulation it becomes quite insoluble, but dissolves like albumin in caustic alkalis. Carbonic and sulphurous acids blacken the red solution; oxygen, or atmospheric air, heightens its colour; protoxide of nitrogen

it purple; while sulphuretted hydrogen, or an alkaline sulphide, it to a dirty greenish black.

tosin differs from the other animal principles in containing as an es- ingredient a remarkable substance not found elsewhere in the animal viz., the oxide of the metal iron. If a little of the dried clot of blood ned in a crucible and digested with dilute hydrochloric acid, a solution obtained rich in oxide of iron; or if the solution of colouring matter ferred to be treated with excess of chlorine gas, the yellow liquid d from the greyish coagulum formed will be found to give in a striking the well-known reactions of the sesquioxide of iron. There is little ither about the condition of the metal; sesquioxide of iron is with- from the dry clot by the cautious addition of sulphuric acid, and much alteration of the colour of the mass.[1] It is well known that organic matters, as tartaric acid, prevent the precipitation of sesqui- iron by alkalis, and its recognition by ferrocyanide of potassium, is very likely that the blood may contain a substance or substances of doing the same.

tosin, necessarily in a modified state, contains, according to Mulder, arts:—

Carbon	65·3
Hydrogen	5·4
Nitrogen	10·4
Oxygen	11·9
Iron	7·0
	100·0

ollowing table represents the composition of healthy human blood as ; it is on the authority of M. Lecanu.[2]

	(1.)	(2.)
	780·15	785·58
	2·10	3·57
ain	65·09	69·41
ring matter	133·00	119·63
allizable fat	2·43	4·30
fat	1·31	2·27
ctive matter of uncertain nature, soluble in water and alcohol	1·79	1·92
ain in combination with soda	1·26	2·01
des of sodium and potassium; carbonates, sphates, and sulphates of potassa and soda...	8·37	7·30
nates of lime and magnesia; phosphates of e, magnesia, and iron; sesquioxide of iron...	2·10	1·42
	2·40	2·59
	1000·00	1000·00

lthy individuals of different sexes these proportions are found to vary the fibrin and colouring matter being usually more abundant in the n in the female; in disease, variations of a far wider extent are often t.

pears singular that the red corpuscles, which are so easily dissolved r, should remain uninjured in the fluid portion of the blood. This artly due to the presence of saline matter, and partly to that of albu-

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[1] g, *Handwörterbuch*, i. 885.

[2] Ann. Chim. et de Phys. xlviii. 320.

min, the corpuscles being alike insoluble in a strong solution of salt and in a highly albuminous liquid. In the blood the limit of dilution within which the corpuscles retain their integrity appears to be nearly reached, for when water is added they immediately become attacked.

Closely connected with the subject of the composition of the blood are those of respiration, and of the production of animal heat.

The simplest view that can be taken of a respiratory organ in an air-breathing animal, is that of a little membranous bag, saturated with moisture, and containing air, over the surface of which meanders a minute blood-vessel, whose contents, during their passage, are thus subjected to the chemical action of the air through the substance of the membranes, and in virtue of the solubility of the gaseous matter itself in the water with which the membranes are imbued. In some of the lower classes of animals, where respiration is sluggish and inactive, these air-cells are few and large; but in the higher kinds they are minute, and greatly multiplied in number, in order to gain extent of surface, each communicating with the external air by the windpipe and its ramifications.

Respiration is performed by the agency of the muscles which lie between and about the ribs, and by the diaphragm. The lungs are not nearly emptied of air at each expiration. Under ordinary circumstances about 15 cubic inches only are thrown out, while by a forced effort as much as 50 or 60 cubic inches may be expelled. This is repeated about 18 times per minute when the individual is tranquil and undisturbed.

The expired air is found to have undergone a remarkable change: it is loaded with aqueous vapour, while a very large proportion of oxygen has disappeared, and its place been supplied by carbonic acid: air *once* breathed containing enough of that gas to extinguish a taper. The total volume of the air seems to undergo but little change in this process, the carbonic acid being about equal to the oxygen lost. This, however, is found to depend very much upon the nature of the food; it is likely that when fatty substances, containing much hydrogen, are used in large quantities, a disappearance of oxygen will be observed. Nitrogen is in small quantity exhaled from the blood. In health no nitrogen is absorbed; the food invariably containing more of that element than the excretions.

Whatever may be the difficulties attending the investigation of these subjects,—and difficulties there are, as the discrepant results of the experiments prove,—one thing is clear: namely, that quantities of hydrogen and carbon are daily oxidized in the body by the free oxygen of the atmosphere, and their products expelled from the system in the shape of water and carbonic acid. Now, if it be true that the heat developed in the act of combination is a constant quantity, and no proposition appears more reasonable, the high temperature of the body may be the simple result of this exertion of chemical force.

The oxidation of combustible matter in the blood is effected in the capillaries of the whole body, not in the lungs, the temperature of which does not exceed that of the other parts. The oxygen of the air is taken up in the lungs, and carried by the blood to the distant capillary vessels; by the aid of which, secretion, and all the mysterious functions of animal life, are undoubtedly performed: here the *combustion* takes place, although how this happens, and what the exact nature of the combustible may be, beyond the simple fact of its containing carbon and hydrogen, yet remains a matter of conjecture. The carbonic acid produced is held in solution by the now venous blood, and probably confers, in great measure, upon the latter its dark colour and deleterious action upon the nervous system. Once more poured into the heart, and by that organ driven into the second set of capillaries bathed with atmospheric air, this carbonic acid is conveyed outwards

through the wet membrane, by a kind of *false diffusion*, constantly observed under such circumstances; while at the same time oxygen is, by similar means, carried inwards, and the blood resumes its bright red colour, and its capability of supporting life. Much of this oxygen is, no doubt, simply dissolved in the serum; the corpuscles, according to Professor Liebig, act as carriers of another portion, in virtue of the iron they contain, that metal being alternately in the state of sesquioxide, and of carbonate of the protoxide,—of sesquioxide in the arteries, and of carbonate of protoxide in the veins, by loss of oxygen, and acquisition of carbonic acid. M. Mulder considers the fibrine to act in the same manner; being true fibrin in the veins, and, in part at least, an oxide of proteine in the arteries.

It would be very desirable to show, if possible, that the quantity of combustible matter daily burned in the body is adequate to the production of the heating effects observed. Something has been done with respect to the carbon. Comparison of the quantities and composition of the food consumed by an individual in a given time, and of the excretions, shows an excess of carbon in the former over the latter, amounting, in some cases, according to Liebig's high estimate,[1] to 14 ounces; the whole of which is thrown off in the state of carbonic acid, from the lungs and skin, in the space of twenty-four hours. This statement applies to the case of healthy, vigorous men, much employed in the open air, and supplied with abundance of nutritious food. Females, and persons of weaker habit, who follow in-door pursuits in warm rooms, consume a much smaller quantity; their respiration is less energetic and the heat generated less in amount. Those who inhabit very cold countries are well known to consume enormous quantities of food of a fatty nature, the carbon and hydrogen of which are, without doubt, chiefly employed in the production of animal heat. These people live by hunting; the muscular exertion required quickens and deepens the breathing; while, from the increased density of the air, a greater weight of oxygen is taken into the lungs, and absorbed into the blood at each inspiration. In this manner the temperature of the body is kept up, notwithstanding the piercing external cold; a most marvellous adjustment of the nature of the food, and even of the inclinations and appetite of the man, to the circumstances of his existence, enable him to bear with impunity an atmospheric temperature which would otherwise injure him.

The carbon consumed in respiration in one day by a horse moderately fed, amounted, in a valuable experiment of M. Boussingault, to 77 ounces; that consumed by a cow, to 70 ounces. The determination was made in the manner just mentioned, viz., by comparing the quantity and composition of the food.

Chyle.—A specimen, examined by MM. Tiedemann and Gmelin, taken from the thoracic duct of a horse, was found closely to resemble, in composition and properties, ordinary blood; the chief difference was the comparative absence of colouring matter, the chyle having merely a reddish-white tint. It coagulated, after standing four hours, and gave a red-coloured clot, small in quantity, and a turbid, reddish-yellow serum. The milky appearance of chyle is due to fat globules, which sometimes confer the same character upon the serum of blood.

Lymph.—Under the name of lymph, two or more fluids, very different in their nature, have been confounded, namely, the fluid taken up by the absorbents of the alimentary canal, which is simply chyle, containing both fibrin and albumin, and the fluid poured out, sometimes in prodigious quantities, from serous membranes, which is a very dilute solution of albumin, contain

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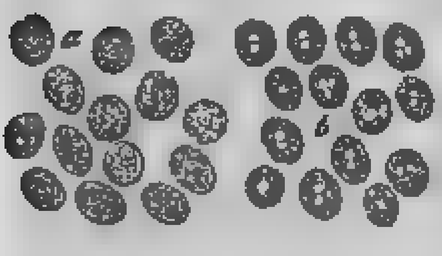
[1] Animal Chemistry, p. 14.

ing a portion of soluble salts of the blood. The *liquor amnii* of the pregnant female, and the fluid of dropsy, are of this character.

MUCUS AND PUS.—The slimy matter effused upon the surface of various mucous membranes, as the lining of the alimentary canal, that of the bladder, of the nose, lungs, &c., to which the general name *mucus* is given, probably varies a good deal in its nature in different situations. It is commonly either colourless or slightly yellow, and translucent or transparent, it is quite insoluble in water, forming, in the moist state, a viscid, gelatinous mass. In dilute alkalis it dissolves with ease, and the solution is precipitated by an addition of acid.

Pus, the natural secretion of a wounded or otherwise injured surface, is commonly a creamy, white, or yellowish liquid, which, under the microscope, appears to consist of multitudes of minute globules (fig. 175, *a*): dilute acetic acid renders them transparent, and shows the internal nuclei (*b*). It is neither acid nor alkaline. Mixed with water, it communicates a milkiness to the latter, but after a time subsides. Caustic alkali does not dissolve pus, but converts it into a transparent, gelatinous substance, which can be drawn out into threads. The peculiar *ropiness* thus produced with an alkali is not peculiar to pus. Healthy mucous owes its sliminess to an alkaline fluid acting on the mucous globules.

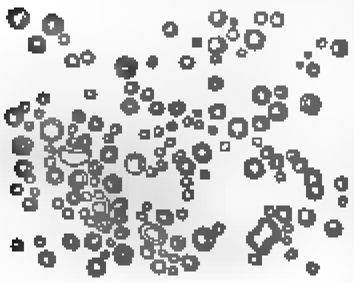
Fig. 175.



MILK, BILE, URINE, AND URINARY CALCULI.

MILK.—The peculiar special secretion destined for the nourishment of the young is, so far as is known, very much the same in flesh-eating animals and in those which live exclusively on vegetable food. The proportions of the constituents may, however, sometimes differ to a considerable extent. It will be seen hereafter that the substances present in milk are wonderfully adapted to its office of providing materials for the rapid growth and development of the animal frame. It contains an azotized matter, casein, nearly identical in composition with muscular flesh, fatty principles, and a peculiar sugar, and lastly, various salts, among which may be mentioned phosphate of lime, held in complete solution in a slightly alkaline liquid. This last is especially important to a process then in activity, the formation of bone.

Fig. 176.



The white, and almost opaque, appearance of milk is an optical illusion; examined by a microscope of even moderate power, it is seen to consist of a perfectly transparent fluid, in which float about numbers of transparent globules (fig. 176), these consist of fat, surrounded by an albuminous envelope, which can be broken mechanically, as in churning, or dissolved by the chemical action of caustic potassa, after which, on agitating the milk with ether, the fat can be dissolved.

When milk is suffered to remain at rest some hours, at the ordinary temperature of the air, a large proportion of the fat globules collect at the surface into a layer of *cream*; if this be now removed and exposed for some time to strong agitation, the fat-globules coalesce into a mass, and the remaining watery liquid is expelled from between them and separated. The *butter* so produced must be thoroughly washed with cold water, to remove as far as possible the last traces of casein, which readily putrefies, and would in that case spoil the whole. A little salt is usually added.

Ordinary butter [illegible] contains some [illegible] when intended for keeping [illegible] The watery part [illegible] matter. [illegible] The consistence of butter [illegible] is dependent upon [illegible] food; in summer [illegible] in winter. The [illegible] referred to.

The casein of milk [illegible] important article of food. [illegible] and coagulated by rennet [illegible] the curd is carefully separated [illegible] proportion of salt and sometimes [illegible] to strong and increasing pressure. [illegible] constantly kept [illegible] fermentation, very little understood [illegible] communicate a particular taste and odour. [illegible] as much of the difference in flavour [illegible] depends in great measure upon the [illegible] considerable quantity of fat and are made with new milk; the inferior descriptions are made with skimmed milk.

Some of the Tartar tribes prepare a kind of spirit from milk by suffering it to ferment, with frequent agitation. The casein converts a part of the milk-sugar into lactic acid and another part into grape-sugar, which in turn becomes converted into alcohol. Mare's milk is said to answer better for this purpose than that of the cow.

In a fresh state, and taken from a healthy animal, milk is always feebly alkaline. When left to itself it very soon becomes acid, and is then found to contain lactic acid, which cannot be discovered in the fresh condition. The alkalinity is due to the soda which holds the casein in solution. In this soluble form casein possesses the power of taking up and retaining a very considerable quantity of phosphate of lime. The density of milk varies exceedingly: its quality usually bears an inverse ratio to its quantity. From an analysis of cow-milk in the fresh state by M. Haidlen,[1] the following statement of its composition in 1000 parts has been deduced:—

Water	873·00
Butter	30·00
Casein	48·20
Milk-sugar	43·90
Phosphate of lime	2·31
" magnesia	0·42
" iron	0·07
Chloride of potassium	1·44
Sodium	0·24
Soda in combination with casein	0·42
	1000·00

Human milk is remarkable for the difficulty with which it coagulates; it generally contains a larger proportion of sugar than cow milk, but scarcely differs in other respects.

Bile.—This is a secretion of a very different character from the preceding; the largest internal organ of the body, the liver, is devoted to its

[1] Annalen der Chemie und Pharmacie, [illegible]

preparation, which is said to take place from venous, instead of arterial blood. The composition of the bile has been made the subject of much investigation: the following is a summary of the most important facts which have been brought to light.

In its ordinary state, bile is a very deep yellow, or greenish, viscid, transparent liquid, which darkens by exposure to the air, and undergoes changes which have been yet imperfectly studied. It has a disagreeable odour, a most nauseous, bitter taste, a distinctly alkaline reaction, and is miscible with water in all proportions. When evaporated to dryness at 212° (100°C), and treated with alcohol, the greater part dissolves, leaving behind an insoluble jelly of mucus of the gall-bladder. This alcoholic solution contains colouring-matter and cholesterin: from the former it may be freed by digestion with animal charcoal, and from the latter by a large admixture of ether, in which the bile is insoluble, and separates as a thick, syrupy, and nearly colourless liquid. The colouring-matter may also be precipitated by baryta-water.

Pure bile thus obtained, when evaporated to dryness by a gentle heat, forms a slightly yellowish brittle mass, resembling gum-Arabic. It is completely soluble in water and absolute alcohol. The solution is not affected by the vegetable acids; hydrochloric and sulphuric acids, on the contrary, give rise to turbidity, either immediately or after a short interval. Acetate of lead partially precipitates it: the tribasic acetate precipitates it completely; the precipitate is readily soluble in acetic acid, in alcohol, and to a certain extent in excess of acetate of lead. When carbonized by heat, and incinerated, bile leaves between 11 and 12 per cent. of ash, consisting chiefly of carbonate of soda, with a little common salt and alkaline phosphate. The recent beautiful researches of Strecker, show that bile is essentially a mixture of the soda-salts of two peculiar conjugate acids very distinctly resembling the resinous and fatty acids. One of these contains nitrogen, but no sulphur, and is termed *cholic acid*, or better, *glycho-cholalic*, being a conjugated compound of a *non-nitrogenous acid*, *cholalic acid*,[1] with the nitrogenetted substance *glycocine* (see page 501), the other containing nitrogen and sulphur, has received the name *choleic acid*, or better, *tauro-cholalic acid*, being a conjugated compound of the same *cholalic acid* with a body to be presently described under the name of *taurin*, containing both nitrogen and sulphur. The relative proportion in which these acids occur in bile, remains pretty constant with the same animal, but varies considerably with different classes of animals.

GLYCO-CHOLALIC ACID may be thus obtained: — When ox bile is perfectly dried and extracted with cold absolute alcohol, and after filtration is mixed with ether, it first deposits a brownish tough resinous mass, and after some time, stellated crystals which consist of glyco-cholalate of soda and potassa. These mixed crystals were first obtained by Platner, and they compose his so called crystallized bile.

Glyco-cholalic acid may be obtained by decomposing the glyco-cholalate of soda by sulphuric acid; it crystallizes in fine white needles of a bitterish sweet taste, is soluble in water and alcohol, but only slightly in ether, and has a strong acid reaction. It is represented by the formula $C_{52}H_{42}NO_{11}.HO$. When boiled with a solution of potassa, the acid divides into cholalic acid $C_{48}H_{39}O_9.HO$, and glycocine or gelatin-sugar: —

$$\underbrace{C_{52}H_{42}NO_{11}.HO}_{\text{Glyco cholalic acid.}}+2HO = \underbrace{C_{48}H_{39}O_9,HO}_{\text{Cholalic acid.}}+\underbrace{C_4H_5NO_4}_{\text{Glycocine.}}$$

[1] Also called cholic acid by some authors.

Boiled with concentrated sulphuric or hydrochloric acids, it yields likewise glycocine, but instead of cholalic acid, another white amorphous acid, *choloidinic acid* ($C_{48}H_{38}O_9$ = cholalic acid — 1 eq. of water), or if the ebullition has continued for some time, a resinous substance, from its insolubility in water called *dyslysin*, ($C_{48}H_{36}O_6$ = cholalic acid — 4 eq. of water.)

Tauro-cholalic acid is thus procured. Ox bile is freed as far as possible from glyco-cholalic acid by means of neutral acetate of lead, and it is then precipitated by basic acetate of lead, to which a little ammonia is added. The precipitate is decomposed by carbonate of soda, when tolerably pure tauro-cholalate of soda is obtained. By decomposing the tauro-cholalate of lead by sulphuretted hydrogen, tauro-cholalic acid is liberated. This substance, however, which was previously called choleic acid and bilin, has never been obtained in the pure state. Its formula, as inferred from the study of its products of decomposition, would be $C_{52}H_{44}NS_2O_{13},HO$. When boiled with alkalis it divides into cholalic acid and taurine:—

$$\underbrace{C_{52}H_{44}NS_2O_{13},HO+2HO}_{\text{Tauro-cholalic acid.}} = \underbrace{C_{48}H_{39}O_9,HO}_{\text{Cholalic acid.}}+\underbrace{C_4H_7NS_2O_6}_{\text{Taurin.}}$$

With boiling acids it gives likewise taurin, but instead of cholalic acid, either choloidinic acid or dyslysin, according to the duration of the ebullition.

Taurin, $C_4H_7NS_2O_6$, crystallizes in colourless regular hexagonal prisms, which have no odour and very little taste. It is neutral to test-paper, and permanent in the air. When burnt, it gives rise to much sulphurous acid. It contains upwards of 25 per cent. of sulphur. It is easily prepared by boiling purified bile for some hours with hydrochloric acid. After filtration and evaporation, the acid residue is treated with five or six times its bulk of boiling alcohol, from which the taurin separates on cooling.

Cholalic or cholic acid, $C_{48}H_{39}O_9,HO$, crystallizes in tetrahedra. It is soluble in sulphuric acid, and on the addition of a drop of this acid and a solution of sugar (1 part of sugar to 4 parts of water), a purple-violet colour is produced, which constitutes Pettenkofer's test for bile. At 383° (195°C) it loses an atom of water, and is converted into chloloidinic acid, which change, as has been pointed out, is also produced by ebullition with acids.

Cholalic acid is best obtained by boiling the resinous mass precipitated by ether from the alcoholic solution of the bile with a dilute solution of potassa for 24 or 36 hours, till the amorphous potassa-salt that has separated begins to crystallize. The dark-coloured soft mass removed from the alkaline liquid, dissolved in water, and hydrochloric acid added, a little ether causes the deposition of the cholalic acid in crystals.

One of the colouring-matters of the bile forms the chief part of the concretions sometimes met with in the gall-bladders of oxen, and which are much valued by painters in water-colours, as forming a magnificent yellow pigment. It dissolves in caustic alkali without change of colour, and when mixed with excess of nitric acid becomes successively green, blue, violet, red, and eventually yellow. The composition of this substance is unknown. Another colouring-matter is dark green, and is considered by Berzelius, as identical with the pigment of leaves.

According to the researches of Strecker and Gundelach, pigs' bile differs from the bile of other animals. This bile contains an acid, to which the name *hyocholic acid* has been given, which may be prepared in the following manner: — fresh pigs' bile is mixed with a solution of sulphate of soda, the precipitate obtained is dissolved in absolute alcohol, and decolorized by animal charcoal. From this solution ether throws down a soda-salt, yield-

ing, on addition of sulphuric acid, hyocholic acid as a resinous mass, which is dissolved in alcohol and re-precipitated by water.

Hyocholic acid contains $C_{54}H_{43}NO_{10}$. When heated with solutions of the alkalis, the acid undergoes a decomposition perfectly analogous to that of glyco-cholalic acid, hyocholic acid, splitting into glycocine and a crystalline acid, very soluble in alcohol, less so in ether, which has been termed *hyocholalic acid.* This substance contains $C_{50}H_{39}O_7,HO$, and the change is represented by the following equation:—

$$\underbrace{C_{54}H_{43}NO_{10}+2HO}_{\text{Hyocholic acid.}} = \underbrace{C_{50}H_{39}O_7,HO}_{\text{Hyocholalic acid.}} + \underbrace{C_4H_5NO_4}_{\text{Glycocine.}}$$

Hence hyocholic acid might be called *glyco-hyocholalic acid.* When boiled with acids, glyco-hyocholalic acid yields likewise glycocine, but instead of hyocholalic acid, a substance representing the dyslysin of the ordinary bile, which might be termed *hyodyslysin.* The composition of hyodyslyin is $C_{50}H_{38}O_6$=hyocholalic acid — 2 eq. HO.

Pigs' bile contains a very trifling quantity of sulphur, probably in the form of a sulphuretted acid corresponding to the tauro-cholalic acid of ox-bile. *Strecker* believes this acid to contain $C_{54}H_{45}NS_2O_{12}$: it might be called *tauro-hyocholalic acid*, which when boiled with an alkali would yield taurin and hyocholalic acid. The sulphuretted acid must be present in pigs' bile in very minute quantity; it is even less known than tauro-cholalic acid.

The once celebrated *oriental bezoar-stones* are biliary calculi, said to be procured from a species of antelope; they have a brown tint, a concentric structure, and a waxy appearance, and consist essentially of a peculiar and definite crystallizable principle called *lithofellinic acid.* To procure this substance, the calculi are reduced to powder and exhausted with boiling alcohol; the dark solution is decolorized by animal charcoal, and left to evaporate by gentle heat, whereupon the lithofellinic acid is deposited in small, colourless, transparent six-sided prisms. It is insoluble in water, and with difficulty soluble in ether, but dissolves with ease in alcohol: it melts at 202° (95°·5C), and at a higher temperature burns with a smoky flame, leaving but little charcoal. Lithofellinic acid dissolves without decomposition in concentrated acetic acid, and in oil of vitriol; it forms a soluble salt with potassa, and dissolves also in ammonia, but crystallizes out unchanged on evaporation. By analysis, lithofellinic acid is found to consist of $C_{40}H_{35}O_7,HO$.

URINE. — The urine is the great channel by which the azotized matter of those portions of the body which have been taken up by the absorbents is conveyed away and rejected from the system in the form of urea. It serves also to remove superfluous water, and foreign soluble matters which get introduced into the blood.

The two most remarkable and characteristic constituents of urine, urea and uric acid, have already been fully described; in addition to these, it contains sulphates, chlorides, phosphates of lime, and magnesia, alkaline salts, and certain yet imperfectly known principles, including an odoriferous and a colouring substance (see foot-note to p. 513).

Healthy human urine is a transparent, light amber-coloured liquid, which, while warm, emits a peculiar, aromatic, and not disagreeable odour. This is lost on cooling, while the urine at the same time occasionally becomes turbid from a deposition of urate of ammonia, which re-dissolves with slight elevation of temperature. It is very decidedly acid to test-paper;[1] this acidity has been ascribed to acid phosphate of soda, to free uric acid, and

[1] The degree of acidity appears to be constantly changing. See Philosophical Trans. 1849.

no free lactic acid; lactic acid can, however, hardly co-exist with urate of ammonia, and the amorphous buff-coloured deposit obtained from fresh urine by spontaneous evaporation *in vacuo* is not uric acid, but the ammonia-salt of that substance, modified as to crystalline form by the presence of minute quantities of chloride of sodium. That a free acid is sometimes present in the urine, is certain; in this case, the reaction to test-paper is far stronger, and the liquid deposits on standing little, red, hard crystals of uric acid; but this is no longer a normal secretion.

An alkaline condition of the urine from fixed alkali is sometimes met with. Such alkalinity can always be induced by the administration of neutral potassa or soda-salts of a vegetable acid, as tartaric or acetic acid; the acid of the salt is burned in the blood in the process of respiration, and a portion of the base appears in the urine in the state of carbonate. The urine is often alkaline in cases of retention, from carbonate of ammonia produced by putrefaction in the bladder itself; but this is easily distinguished from alkalinity from fixed alkali, in which it is *secreted* in that condition.

The density of the urine varies from 1·005 to 1·030; about 1·020 to 1·023 may be taken as the average specific gravity. A high degree of density in urine may arise from an unusually large proportion of urea; in such a case, the addition of nitric acid will occasion an almost immediate production of crystals of nitrate of urea, whereas with urine of the usual degree of concentration many hours will elapse before the nitrate begins to separate. The quantity passed depends much upon circumstances, as upon the activity of the skin; it is usually more deficient in quantity and of higher density in summer than in winter. Perhaps about 32 ounces in the 24 hours may be assumed as a mean.

When kept at a moderate temperature, urine, after some days, begins to decompose; it exhales an offensive odour, becomes alkaline from the production of carbonate of ammonia, and turbid from the deposition of earthy phosphates. The carbonate of ammonia is due to the putrefactive decomposition of the urea, which gradually disappears, the *ferment*, or active agent of the change, being apparently the mucus of the bladder, a portion of which is always voided with the urine. It has been found also that the yellow adhesive deposit from stale urine is a most powerful ferment to the fresh secretion. In this putrefied state urine is used in several of the arts, as in dyeing; and forms, perhaps, the most valuable manure for land known to exist.

Putrid urine always contains a considerable quantity of sulphide of ammonium; this is formed by the de-oxidation of sulphates by the organic matter. The highly offensive odour and extreme pungency of the decomposing liquid may be prevented by previously mixing the urine, as Liebig suggests, with sulphuric or hydrochloric acid, in sufficient quantity to saturate all the ammonia that can be formed.

The following is an analysis of human urine, by Berzelius. 1000 parts contained

Water	933·00
Urea	30·10
Lactates and extractive matter[1]	17·14

[1] All dark-coloured, uncrystallizable substances, soluble both in water and alcohol, were confounded by the old chemists under the general name of *extractive matter*. The progress of modern science constantly tends to extricate from this confused mass one by one the many definite organic principles therein contained in a more or less modified form, and to restrict within narrower limits the application of the term. In the above instance, the colouring matter of the urine, and it may be several other substances, are involved.

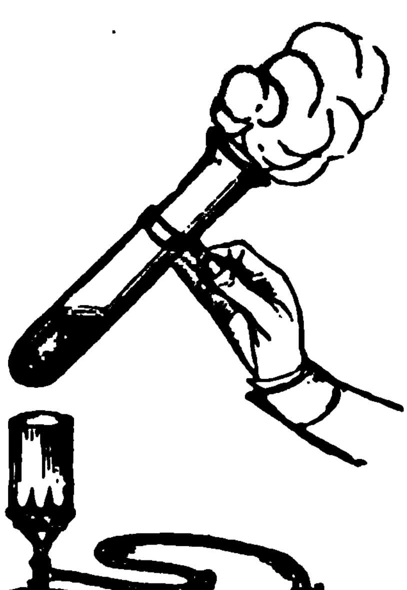
Professor Liebig states that all his endeavours to obtain direct evidence of the existence of lactic acid in the urine, either in a fresh or putrid state, completely failed. Putrid urine

Uric acid	1·00
Sulphates of potassa and soda	6·87
Phosphate of soda	2·92
" ammonia	1·65
" lime and magnesia	1·00
Chloride of sodium	4·45
Sal-ammoniac	1·50
Silica	0·03
Mucus of bladder	0·32
	1000·00

In certain states of disorder and disease substances appear in the urine which are never present in the normal secretion; of these the most common is albumin. This is easily detected by the addition of nitric acid in excess, which then causes a white cloud or turbidity, which is permanent when boiled, or by corrosive sublimate, the urine being previously acidified by a little acetic acid; boiling causes usually a precipitate which is not dissolved by a drop or two of acid. Mere turbidity by boiling is no proof of albumin; the earthy phosphates being often thrown down from nearly neutral urine under such circumstances; the phosphatic precipitate is, however, instantly dissolved by a drop of nitric acid.

In *diabetes* the urine contains grape-sugar, the quantity of which commonly increases with the progress of the disease, until it becomes enormous, the urine acquiring a density of 1·040 and beyond. It does not appear that the urea is deficient *absolutely*, although more difficult to discover from being mixed with such a mass of syrup. The smallest trace of sugar may be discovered in urine by Trommer's test, (fig. 177,) formerly mentioned: a few drops of solution of sulphate of copper are added to the urine, and afterwards an excess of caustic potassa; if sugar be present, a deep-blue liquid results, which, on boiling, deposits red suboxide of copper. With proper management, this test is very valuable; it will even detect sugar in the blood of diabetic patients.[1] Urine containing sugar, when mixed with a little yeast, and put in a warm place, readily undergoes vinous fermentation, and afterwards yields, on distillation, weak alcohol, contaminated with ammonia.

Fig. 177.



The urine of children is said sometimes to contain benzoic acid; it is possible that this may be hippuric acid. When benzoic acid is taken, the urine after a few hours yields on concentration, and the addition of hydrochloric acid, needles of hippuric acid, soiled by adhering uric acid.

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yielded a volatile acid in a notable quantity, which turned out to be acetic acid; a little benzoic acid was also noticed, and traced to a small amount of hippuric acid in the recent urine. The acid reaction of urine is ascribed to an acid phosphate of soda, produced by the partial decomposition of some of the common phosphate, the reaction of which is alkaline, by the organic acids (uric and hippuric) generated in the system, aided by the sulphuric acid constantly produced by the oxidation of the protein-compounds of the food, or rather of the body.—*Lancet, June*, 1844.

Still more recently Liebig has announced the discovery in the urine of kreatin and kreatinine, already described. Putrid urine contains kreatinine only.

[1] Dr. Bence Jones, Med. Chirur. Trans. vol. xxvi. Great care must be taken in using this test, which depends on the instantaneous reduction of the oxide of copper. By long boiling very many organic substances produce this reaction.

eposit of buff-coloured or pinkish amorphous urate of ammonia, frequently occurs in urine upon cooling, after unusual exercise or rangements of health, may be at once distinguished from a deposit nio-magnesian phosphate by its instant disappearance on the appli- f heat. The earthy phosphates, besides, are hardly ever deposited ine which has an acid reaction. The nature of the red colouring which so often stains urinary deposits, especially in the case of free , is yet unknown.

ellow principle of bile has been observed in urine in severe cases of .

rine of the carnivorous mammifera is small in quantity, and highly has a very offensive odour, and quickly putrefies. In composition bles that of man, and is rich in urea. In birds and serpents the a white pasty substance, consisting almost entirely of urate of ammo- herbivorous animals it is alkaline and often turbid from earthy car- and phosphates; urea is still the characteristic ingredient, while of there is scarcely a trace; hippuric acid is usually, if not always, sometimes to a very large extent. When the urine putrefies, this acid, as already noticed, becomes changed to benzoic acid.

RY CALCULI.—Stony concretions, differing much in physical charac- in chemical composition, are unhappily but too frequently formed adder itself, and give rise to one of the most distressing complaints humanity is subject. Although many endeavours have been made ome solvent or solvents for these calculi, and thus supersede the of a formidable surgical operation for their removal, success has very partial and limited.

y calculi are generally composed of concentric layers of crystalline hous matter, of various degrees of hardness. Very frequently the oint or nucleus is a small foreign body; curious illustrations of this seen in any large collection. Calculi are not confined to man; the imals are subject to the same affliction; they have been found in xen, sheep, pigs, and almost constantly in rats.

llowing is a sketch of the principal characters of the different varie- alculi:—

c Acid.—These are among the most common; externally they are r warty, of yellowish or brownish tint; ve an imperfectly crystalline, dis- oncentric structure, and are tolerably ig. 178. Before the blowpipe the uric alus burns away, leaving no ash. It ble in water, but dissolves with facility c potassa, with but little ammoniacal he solution mixed with acid gives a white curdy precipitate of uric acid, eedily becomes dense and crystalline. ly heated with nitric acid, and then ith a little ammonia, it gives the cha- c reaction of uric acid, viz., deep pur- murexide.

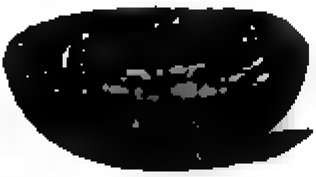
Fig. 178.

Fig. 179.

te of Ammonia.—Calculi of urate of much resemble the preceding; they ly distinguished, however. Fig. 179. der boiled in water dissolves, and the gives a precipitate of uric acid when ith *hydrochloric* acid. It dissolves ot *carbonate* of potassa with copious of ammonia.

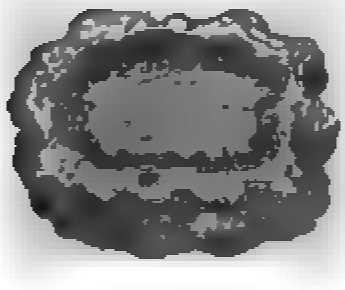
3. *Fusible Calculus; Phosphate of Lime with Phosphate of Magnesia and Ammonia.*—This is one of the most common kinds. The stones are usually white or pale-coloured, smooth, earthy, and soft; they often attain a large size. Fig. 180. Before the blowpipe this substance blackens from animal matter which earthy calculi always contain; then becomes white, and melts to a bead with comparative facility. It is insoluble in caustic alkali, but readily soluble in dilute acids, and the solution is precipitated by ammonia. Calculi of unmixed phosphate of lime are rare, as also those of phosphate of magnesia and ammonia; the latter salt is sometimes seen forming small, brilliant crystals in cavities in the fusible calculus.

Fig. 180.



4. *Oxalate of Lime Calculus; Mulberry Calculus.*—The latter name is derived from the rough, warty character, and dark blood-stained aspect of this variety; it is perhaps the worst form of calculus. Fig. 181. It is exceedingly hard; the layers are thick and imperfectly crystalline. Before the blowpipe the oxalate of lime burns to carbonate by a moderate red-heat, and, when the flame is strongly urged, to quicklime. It is soluble in moderately strong hydrochloric acid by heat, and very easily in nitric acid. When finely powdered and long boiled in a solution of carbonate of potassa, oxalate of potassa may be discovered in the filtered liquid, when carefully neutralised by nitric acid, by white precipitates with solutions of lime, lead, and silver. A sediment of oxalate of lime in very minute, transparent, octahedral crystals, only to be seen by the microscope, is of common occurrence in urine in which a tendency to urate of ammonia deposits exists.

Fig. 181.



5. *Cystic and Xanthic Oxides* have already been described: they are very rare, especially the latter. Calculi of cystic oxide are very crystalline, and often present a waxy appearance externally; sediments of cystic oxide are sometimes met with. As before mentioned, this substance is a definite crystallizable organic principle, containing sulphur to a large amount; it is soluble both in acids and alkalis. When the solution in nitric acid is evaporated to dryness, it blackens; when dissolved in a large quantity of caustic potassa, a drop of solution of acetate of lead added, and the whole boiled, a black precipitate containing sulphide of lead makes its appearance. By these characters cystic oxide is easily recognized.

Xanthic oxide, also a definite organic principle, is distinguished by the peculiar deep-yellow colour produced when its solution in nitric acid is evaporated to dryness; it is soluble in alkalis, but not in hydrochloric acid.

Very many calculi are of a composite nature, the composition of the different layers being occasionally changed, or alternating; thus, urate of ammonia and oxalate of lime are not unfrequently associated in the same stone.

NERVOUS SUBSTANCE; MEMBRANOUS TISSUE; BONES.

NERVOUS SUBSTANCE. — The brain and nerves consist of an albuminous substance, containing several remarkable fatty principles, capable of being extracted by alcohol and ether, some of which are yet very imperfectly known, and about 80 per cent. of water. Besides cholesterin, and a little ordinary fat, separated in the manner mentioned, M. Frémy describes two

new bodies,[1] *cerebric acid* and *oleo-phosphoric acid*. The first is solid, white, and crystalline, soluble without difficulty in boiling alcohol, and forming with hot water a soft, gelatinous mass. It melts when heated, and decomposes almost immediately afterwards, exhaling a peculiar odour, and leaving a quantity of charcoal which contains free phosphoric acid, and is in consequence very difficult to burn. It combines with the alkalis, but forms insoluble compounds. Cerebric acid contains in 100 parts—

Carbon	66·7
Hydrogen	10·6
Nitrogen	2·3
Oxygen	19·5
Phosphorus	0·9
	100·0

The oleo-phosphoric acid has been even less perfectly studied than the preceding substance. It is of soft oily consistence, soluble in hot alcohol and ether, and saponifiable. When boiled with water, it is resolved into a fluid neutral oil, called *cerebrolein*, and phosphoric acid, which dissolves.

The oily matter of the brain is sufficient in quantity to form with the albuminous portion a kind of emulsion, which, when beaten up, remains long suspended in water.

MEMBRANOUS TISSUES; SKIN.—The composition of the many gelatin-giving tissues of the body is in great measure unknown; even that of gelatin itself is very doubtful, as several different substances may very possibly be confounded under this name. Dr. Scherer[2] has given, among many others, analyses of the middle coat of the arteries, which will serve as an example of a finely organized, highly elastic membrane, and of the coarse epidermis of the sole of the foot, with which it may be contrasted:—

	Artery coat.	Epidermis.
Carbon	53·75	51·04
Hydrogen	7·08	6·80
Nitrogen	15·36	17·23
Oxygen	23·81	24·93
	100·00	100·00

A little sulphur was found in the epidermis. Hair, horn, nails, wool, and feathers have a nearly similar composition; they all dissolve with disengagement of ammonia in caustic potassa, and the solution, when mixed with acid, deposits a kind of protein common to the whole. It is useless assigning formulæ to substances yet so little understood.

The principle of tanning, of such great practical value, is easily explained. When the skin of an animal, carefully deprived of hair, fat, and other impurities, is immersed in a dilute solution of tannic acid, the animal matter gradually combines with that substance as it penetrates inwards, forming a perfectly insoluble compound, which resists putrefaction completely; this is leather. In practice, lime-water is used for cleansing and preparing the skin, and an infusion of oak-bark, or sometimes catechu, or other astringent matter, for the source of tannic acid. The process itself is necessarily a slow one, as dilute solutions only can be safely used. Of late years, however, various contrivances, some of which show great ingenuity, have been adopted with more or less success, for quickening the operation. All leather is not tanned; glove-leather is dressed with alum and common salt, and

[1] Ann. Chim. et Phys. 3rd series, ii. 463.
[2] Annalen der Chemie und Pharmacie, xl. 50.

afterwards treated with a preparation of the yolks of eggs, which contain an albuminous matter and a yellow oil. Leather of this kind still yields a size by the action of boiling water.

BONES. — Bones are constructed of a dense cellular tissue of membranous matter, made stiff and rigid by insoluble earthy salts, of which phosphate of lime ($3CaO,PO_5$) is the most abundant. The proportions of earthy and animal matter vary very much with the kind of bone and with the age of the individual, as will be seen in the following table, in which the corresponding bones of an adult and of a still-born child are compared:—

	ADULT.		CHILD.	
	Inorganic matter.	Organic matter.	Inorganic matter.	Organic matter.
Femur	62·49	37·51	57·51	42·49
Humerus	63·02	36·98	58·08	41·92
Radius	60·51	39·49	56·50	43·50
Os temporum	63·50	36·50	55·90	44·10
Costa	57·49	42·51	53·75	46·25

The bones of the adult being constantly richer in earthy salts than those of the infant.

The following complete comparative analysis of human and ox-bones is due to Berzelius:—

	Human bones.	Ox-bones.
Animal matter soluble by boiling	32·17	33·30
Vascular substance	1·13	
Phosphate of lime, with a little fluoride of calcium	53·04	57·35
Carbonate of lime	11·30	3·85
Phosphate of magnesia	1·16	2·05
Soda, and a little common salt	1·20	3·45
	100·00	100·00

The teeth have a very similar composition, but contain less animal matter; their texture is much more solid and compact. The enamel does not contain more than 2 or 3 per cent. of animal matter.

ON THE FUNCTION OF NUTRITION IN THE ANIMAL AND VEGETABLE KINGDOMS.

The constant and unceasing waste of the animal body in the process of respiration, and in the various secondary changes therewith connected, necessitates an equally constant repair and renewal of the whole frame by the deposition or organization of matter from the blood, which is thus gradually impoverished. To supply this deficiency of solid material in the circulating fluid is the office of the food. The striking contrast which at first appears in the nature of the food of the two great classes of animals, the vegetable feeders and the carnivorous races, diminishes greatly on close examination: it will be seen, that, so far as the materials of blood, or, in other words, those devoted to the repair and sustenance of the body itself, are concerned, the process is the same. In a flesh-eating animal great simplicity is observed in the construction of the digestive organs: the stomach is a mere enlargement of the short and simple alimentary canal; and the reason is plain: the food of the creature, flesh, is absolutely identical in composition with its own blood, and with the body that blood is destined to nourish. In the stomach it undergoes mere solution, being brought into a state fitted for absorption by the lacteal vessels, by which it is nearly all taken up, and at once conveyed into the blood: the excrements of such animals are little more

an the comminuted bones, feathers, hair, and other matters which refuse dissolve in the stomach. The same condition, that the food employed for e nourishment of the body must have the same or nearly the same chemi-l composition as the body itself, is really fulfilled in the case of animals at live exclusively on vegetable substances. It has been shown[1] that cer-in of the azotized principles of plants, which often abound, and are never together absent, have a chemical composition and assemblage of properties hich assimilate them in the closest manner, and it is believed even identify em, with the azotized principles of the animal body; vegetable albumin, rin, and casein are scarcely to be distinguished from the bodies of the same me extracted from blood and milk.

If a portion of wheaten flour be made into a paste with water, and cau-usly washed on a fine metallic sieve, or in a cloth, a greyish, adhesive, astic, insoluble substance will be left, called *gluten* or *glutin*, and a milky uid will pass through, which by a few hours' rest becomes clear by de-siting a quantity of starch. If now this liquid be boiled, it becomes again rbid from the production of a flocculent precipitate, which, when collected, ashed, dried, and purified from fat by boiling with ether, is found to have e same composition as animal albumin. The glutin itself is a mixture of ue vegetable fibrin, and a small quantity of a peculiar azotized matter lled *gliadin*, to which its adhesive properties are due. The gliadin may extracted by boiling alcohol, together with a thick, fluid oil, which is parable by ether; it is gluey and adhesive, quite insoluble in water, and, hen dry, hard and translucent like horn; it dissolves readily in dilute caus-c alkali, and also in acetic acid. The fibrin of other grain is unaccompa-ed by gliadin; barley and oatmeal yield no glutin, but incoherent filaments nearly pure fibrin.

Vegetable albumin in a soluble state abounds in the juice of many soft cculent plants used for food; it may be extracted from potatoes by mace-ting the sliced tubers in cold water containing a little sulphuric acid. It agulates when heated to a temperature dependent upon the degree of con-ntration, and cannot be distinguished when in this state from boiled white egg in a divided condition.

Almonds, peas, beans, and many of the oily seeds, contain a principle hich bears the most striking resemblance to the casein of milk. When a lution of this substance is heated, no coagulation occurs, but a skin forms n the surface, just as with boiled milk. It is coagulable by alcohol, and by etic acid: the last being a character of importance. Such a solution mixed ith a little sugar, an emulsion of sweet almonds, for instance, left to itself, on becomes sour and curdy, and exhales an offensive smell; it is then found contain lactic acid.

All these substances dissolve in caustic potassa with production of a small antity of alkaline sulphide; the filtered solutions mixed with excess of id give precipitates of protein.

The following is the composition in 100 parts of vegetable albumin and brin; it will be seen that they agree very closely with the results before iven:—

	Albumin.	Fibrin.
Carbon	55·01	54·60
Hydrogen	7·23	7·30
Nitrogen	15·92	15·81
Oxygen, sulphur, and phosphorus	21·84	22·29
	100·00	100·00

[1] Liebig, Ann. der Chem. und Pharm. xxxix. 129.

The composition of vegetable casein, or *legumin*, has not been so well made out; so much discrepancy appears in the analyses as to lead to the supposition that different substances have been operated upon.

The great bulk, however, of the solid portion of the food of the herbivora consists of bodies which do not contain nitrogen, and therefore cannot yield sustenance in the manner described: some of these, as vegetable fibre or lignin, and waxy matter, pass unaltered through the alimentary canal; others, as starch, sugar, gum, and perhaps vegetable fat, are absorbed into the system, and afterwards disappear entirely: they are supposed to contribute very largely to the production of animal heat.

On these principles, Professor Liebig[1] has very ingeniously made the distinction between what he terms *plastic elements of nutrition* and *elements of respiration*; to the former class belong

Vegetable fibrin,
Vegetable albumin,
Vegetable casein,
Animal flesh,
Blood.

To the latter,

Fat,	Grape-sugar,
Starch,	Milk-sugar,
Gum,	Pectine,
Cane-sugar,	Alcohol?

In a flesh-eating animal the waste of the tissues is very rapid, the temperature being, as it were, kept up in great measure by the burning of azotized matter; in a vegetable feeder it is probably not so great, the non-azotized substances being consumed in the blood in the place of the organic fabric.

When the muscular movements of a healthy animal are restrained, a genial temperature kept up, and an ample supply of food containing much amylaceous or oily matter given, an accumulation of fat in the system rapidly takes place; this is well-seen in the case of stall-fed cattle. On the other hand, when food is deficient, and much exercise is taken, emaciation results. These effects are ascribed to difference in the activity of the respiratory function; in the first instance, the heat-food is supplied faster than it is consumed, and hence accumulates in the form of fat; in the second, the conditions are reversed, and the creature is kept in a state of leanness by its rapid consumption. The fat of an animal appears to be a provision of nature for the maintenance of life during a certain period under circumstances of privation.

The origin of fat in the animal body has recently been made the subject of much animated discussion; on the one hand it was contended that satisfactory evidence exists of the conversion of starch and saccharine substances into fat, by separation of carbon and oxygen, the change somewhat resembling that of vinous fermentation: it was argued, on the other side, that oily or fatty matter is invariably present in the food supplied to the domestic animals, and that this fat is merely absorbed and deposited in the body in a slightly modified state. The question has now been decided in favour of the first of these views, which was enunciated by Professor Liebig, by the very chemist who formerly advocated the second opinion. By a series of very beautiful experiments, MM. Dumas and Milne Edwards proved that bees exclusively feeding upon sugar were still capable of producing wax, which was pointed out as a veritable fact.

[1] Animal Chemistry, p. 96.

It is not known in what manner *digestion*, the reduction in the stomach of e food to a nearly fluid condition, is performed. The natural secretion of at organ, the *gastric juice*, is said to contain a very notable quantity of free rdrochloric acid. Dilute hydrochloric acid, aided by a temperature of 98° 6°·6C) or 100° (37°·7C), dissolves coagulated albumin, fibrin, &c.; but any hours are required for that purpose. The gastric secretion has been ipposed to contain a peculiar organic principle called *pepsin*, said to have een isolated, to which this power of dissolving albuminous substances in onjunction with the hydrochloric acid is attributed. In the saliva a pecuar organic principle exists, which causes the conversion of starch into sugar. starch is held in the mouth even for two minutes, this change is found to ccur. The active cause of this change has been looked on as a kind of aniial diastase.

The food of animals, or rather that portion of the food which is destined the repair and renewal of the frame itself, is thus seen to consist of subances identical in composition with the body it is to nourish, or requiring ut little chemical change to become so.

The chemical phenomena observed in the animal system resemble so far iose produced out of the body by artificial means, that they are all, or nearly ll, so far as is known, changes in a descending series; albumin and fibrin re probably more complex compounds than gelatin or the membrane which irnishes it; this, in turn, has a far greater complexity of constitution than rea, the regular form in which rejected azotized matter is conveyed out of ie body. The animal lives by the assimilation into its own substance of the iost complex and elaborate products of the organic kingdom;—products hich are, and, apparently, can only be, formed under the influence of vegeable life.

The existence of the plant is maintained in a manner strikingly dissimilar: he food supplied to vegetables is *wholly inorganic;* the carbonic acid and itrogen of the atmosphere, the water which falls as rain, or is deposited as ew; the minute trace of ammoniacal vapour present in the air; the alkali nd saline matter extracted from the soil;—such are the substances which ield to plants the elements of their growth. That green healthy vegetables o possess, under circumstances to be mentioned immediately, the property f decomposing carbonic acid absorbed by their leaves from the air, or coneyed thither in solution through the medium of their roots, is a fact posiively proved by direct experiment, and rendered certain by considerations f a very stringent kind. To effect this very remarkable decomposition, the ifluence of light is indispensable; the diffuse light of day suffices in some egrees, but the direct rays of the sun greatly exalt the activity of the proess. The carbon separated in this manner is retained in the plant in union rith the elements of water, with which nitrogen is also sometimes associated, rhile the oxygen is thrown off into the air from the leaves in a pure and aseous condition.

The effect of ammoniacal salts upon the growth of plants is so remarkable, s to leave little room for doubt concerning the peculiar function of the amionia recently discovered in the air. Plants which in their cultivated state ontain, and consequently require, a large supply of nitrogen, as wheat, and he cereals in general, are found to be greatly benefited by the application the land of such substances as putrefied urine, which may be looked upon s a solution of carbonate of ammonia, the *guano*[1] of the South Seas, which

[1] Guano is the partially decomposed dung of birds, found in immense quantity on some f the barren islets of the western coast of South America, as that of Peru. More recently, milar deposits have been found on the coast of Southern Africa. The guano now imported ito England from these localities is usually a soft, brown powder, of various shades of lour. White specks of bone-earth, and sometimes masses of saline matter, may be found

usually contains a large proportion of ammoniacal salt, and even of a pure sulphate of ammonia. Some of these manures doubtless owe a part of their value to the phosphates and alkaline salts they contain; still, the chief effect is certainly due to the ammonia.

Upon the members of the vegetable kingdom thus devolves the duty of building up, as it were, out of the inorganic constituents of the atmosphere,—the carbonic acid, the water, and the ammonia,—the numerous complicated organic principles of the perfect plant, many of which are afterwards destined to become the food of animals, and of man. The chemistry of vegetable life is of a very high and mysterious order, and the glimpses occasionally obtained of its general nature are few and rare. One thing, however, is manifest, namely, the wonderful relations between the two orders of organized beings, in virtue of which the rejected and refuse matter of the one is made to constitute the essential and indispensable food of the other. While the animal lives, it exhales incessantly from its lungs, and often from its skin, carbonic acid; when it dies, the soft parts of its body undergo a series of chemical changes of *degradation*, which terminate in the production of carbonic acid, water, carbonate of ammonia, and, perhaps, other products in small quantity. These are taken up by a fresh generation of plants, which may in their turn serve for food to another race of animals.

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in it. That which is most recent, and probably most valuable as manure, often contains undecomposed uric acid, besides much oxalate or hydrochlorate of ammonia, and alkaline phosphates, and other salts; it has a most offensive odour. The specimens taken from old deposits have but little smell, are darker in colour, contain no uric acid, and much less ammoniacal salt, the chief components are bone-earth, a peculiar dark-coloured organic matter, and soluble inorganic salts. See also page 413.

SECTION IX.

ON CERTAIN PRODUCTS OF THE DESTRUCTIVE DISTILLATION AND SLOW PUTREFACTIVE CHANGE OF ORGANIC MATTER.

SUBSTANCES OBTAINED FROM TAR.

THERE are three principal varieties of tar:—(1.) *Tar of the wood-vinegar maker*, procured by the destructive distillation of dry hard wood; (2.) *Stockholm tar*, so largely consumed in the arts, as in ship-building, &c., which is obtained by exposing to a kind of rude *distillatio per descensum* the roots and useless parts of resinous pine and fir-timber; and, lastly, (3.) *Coal* or *mineral tar*, a by-product in the manufacture of coal-gas. This is fluid, black, and ammoniacal.

All these tars yield by distillation, alone or with water, oily liquids of extremely complicated nature, from which a number of curious products, to be presently described, have been procured: the solid brown or black residue constitutes pitch. Hard-wood tar furnishes the following:—

PARAFFIN; TAR-OIL STEARIN.—This remarkable substance is found in that part of the wood-oil which is heavier than water; it is extracted by redistilling the oil in a retort, collecting apart the last portions, gradually adding a quantity of alcohol, and exposing the whole to a low temperature. Thus obtained, paraffin appears in the shape of small, colourless needles, fusible at 110° (43°·3C) to a clear liquid, which on solidifying becomes glassy and transparent. It is tasteless and inodorous; volatile without decomposition; and burns, when strongly heated, with a luminous yet smoky flame. It is quite insoluble in water, slightly soluble in alcohol, freely in ether, and miscible in all proportions, when melted, with both fixed and volatile oils. The most energetic chemical reagents, as strong acids, alkalis, chlorine, &c., fail to exert the smallest action on this substance; it is not known to combine in a definite manner with any other body, whence its extraordinary name, from *parum affinis*.

Paraffin contains carbon and hydrogen only, and in the same proportions as in olefiant gas, or CH. M. Lewy, of Copenhagen, makes it $C_{20}H_{21}$. The rational formula is unknown.

EUPIONE.[1]—This is the chief component of the light oil of wood-tar; it occurs also in the tar of animal matters, and in the fluid product of the distillation of rape-seed oil. Its separation is effected by the agency of concentrated sulphuric acid, or of a mixture of sulphuric acid and nitre, which oxidizes and destroys most of the accompanying substances. In a pure state, it is an exceedingly thin, colourless liquid, of agreeable aromatic odour, but destitute of taste; it is the lightest known liquid, having a density of 0·655. At 116° (46°6C) it boils and distils unchanged. Dropped upon paper, it makes a greasy stain, which after a time disappears. Eupione is very inflammable, and burns with a bright luminous flame. In water it is

[1] *From εὖ, good, beautiful, and πίων, fat.*

quite insoluble, in rectified spirit nearly so, but with ether and oils freely miscible.

Eupione is a hydrocarbon; according to M. Hess it consists of C_5H_6. It is very probable that eupione frequently contains and sometimes entirely consists of hydride of amyl (see page 389).

Other volatile oils, having a similar origin, and perhaps a similar composition, but differing from the above in specific gravity and boiling-point, are sometimes confounded with eupione. The study of these substances presents many serious difficulties. It is even doubtful whether the eupione be not *formed* by the energetic chemical agents employed in its supposed purification, and this remark applies with even greater force to the next three or four tar-products to be noticed.

PICAMAR.[1]—A component of the heavy oil of wood; it is a viscid, colourless, oily liquid, of feeble odour, but intensely bitter taste. Its density is 1·095, and it boils at 518° (270°C). It is insoluble in water, but dissolves in all proportions in alcohol, ether, and the oils. The most characteristic property of picamar is that of forming with the alkalis and ammonia crystalline compounds, which, although decomposed by water, are soluble without change in spirit. The composition of this substance is unknown.

KAPNOMOR.[2]—Such is the name given by Dr. Reichenbach to another oily liquid obtained from the same source as the last, by a long and complex process, in which strong solutions of caustic potassa are freely used. It is described as a colourless volatile oil, of high boiling-point, and rather lighter than water; it has an odour of ginger, and a taste feeble at first, but afterwards becoming connected with an insupportable sense of suffocation. Water refuses to dissolve it; alcohol and ether take it up easily; and oil of vitriol combines with it, giving rise to a complex acid, the potassa-salt of which is crystallizable. Its composition is unknown.

CEDRIRET.[3]—The lighter oil of hard-wood tar contains a substance, separable from the eupione, &c., by caustic alkalis, which in contact with oxidizing agents, as sulphate of sesquioxide of iron, chromic acid, or even atmospheric air, yields a mass of small, red, reticulated crystals, infusible by heat, and soluble in concentrated sulphuric acid with deep indigo-blue colour. This substance is insoluble in water, alcohol, and ether; nothing is known respecting its composition.

KREOSOTE.[4] — This is by far the most important and interesting body of the group; its discovery is due to Dr. Reichenbach; it is the principle to which wood-smoke owes its power of curing and preserving salted meat and other provisions. Kreosote is most abundantly contained in the heavy oil of beech-tar, as procured from the wood-vinegar maker, and is thence extracted by a most tedious and complicated series of operations; it certainly pre-exists, however, in the original material. The tar is distilled in a metallic vessel, and the different products collected apart; the most volatile portion, which is lighter than water, and consists chiefly of eupione, is rejected; the second portion is denser, and contains the kreosote, and is set aside; the distillation is stopped when paraffin begins to pass over in quantity. The impure kreosote is first agitated with carbonate of potassa to remove adhering acid, separated, and re-distilled, the first part being again rejected; it is next strongly shaken with a solution of phosphoric acid, and again distilled; a quantity of ammonia is thus separated. Afterwards, it is dissolved in a solution of caustic potassa of specific gravity 1·12, and de-

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[1] From *pix*, and *amarus*, in allusion to its bitter taste.
[2] From καπνός, smoke, μοῖρα, part.
[3] From *cedrium*, the old name for acid tar-water, and *rete*, a net.
[4] Derived from κρέας, flesh, and σώζω, I preserve.

canted from the insoluble oil which floats on the surface; this alkaline liquid is boiled, and left some time in contact with air, by which it acquires a brown colour from the oxidation of some yet unknown substance present in the crude product. The compound of kreosote and alkali is next decomposed by sulphuric acid: the separated kreosote is again dissolved in caustic potassa, boiled in the air, and the solution decomposed by acid, and this treatment repeated until the product ceases to become coloured by the joint influence of oxygen and the alkaline base. When so far purified, it is well washed with water, and distilled. The first portion contains water; that which succeeds is pure kreosote.

In this condition kreosote is a colourless, somewhat viscid oily liquid, of great refractive and dispersive power. It is quite neutral to test-paper: it has a penetrating and most peculiar odour, that, namely, of smoked meat, and a pungent and almost insupportable taste when placed in a very small quantity upon the tongue. The density of this substance is 1·037, and its boiling-point 397° (202°·8C). It inflames with difficulty, and then burns with a smoky light. When quite pure, it is inalterable by exposure to the air; much of the kreosote of commerce becomes, however, under these circumstances, gradually brown. 100 parts of cold water take up about 1¼ parts of kreosote; at a high temperature rather more is dissolved, and the hot solution abandons a portion on cooling. The kreosote itself absorbs water also to a considerable extent. In acetic acid it dissolves in much larger quantity. Alcohol and ether mix with kreosote in all proportions. Concentrated sulphuric acid, by the aid of heat, blackens and destroys it. Caustic potassa dissolves kreosote with great facility, and forms with it a definite compound, which crystallizes in brilliant pearly scales.

Kreosote consists of carbon, hydrogen, and oxygen, but its exact composition is yet uncertain. The formula $C_{14}H_8O_2$ has been given.

The most remarkable and characteristic feature of the compound in question is its extraordinary antiseptic power. A piece of animal flesh steeped in a very dilute solution of kreosote dries up to a mummy-like substance, but absolutely refuses to putrefy. The well-known efficacy of impure wood-vinegar in preserving provisions is with justice attributed to the kreosote it contains; and the effect of mere wood-smoke is also thus explained. In a pure state, kreosote is sometimes employed by the dentist for relieving toothache arising from putrefactive decay in the substance of the tooth.

Chrysen and pyren. — M. Laurent extracted from pitch, by distillation at a high temperature, two new solid bodies, to which he gave the preceding names; they condense together, with a quantity of oily matter, partly in the neck of the retort, and partly in the receiver, and are separated by the aid of ether. *Chrysen*, so called from its golden colour, is a pure yellow, crystalline powder, which fuses by heat, and sublimes without much decomposition. It is insoluble in water and alcohol, and nearly insoluble in ether: warm oil of vitriol dissolves it, with the development of a beautiful deep-green colour. Boiling nitric acid converts it into an insoluble red substance, which has not been studied. Chrysen is composed of C_3H.

Pyren differs from the preceding substance in being colourless, crystallizing in small, soft, micaceous scales, soluble in boiling alcohol and ether. It is fusible and volatile. Pyren contains C_5H_2.

Oil of ordinary tar, obtained by distillation alone, or with water, consists in great measure of unaltered oil of turpentin, mixed, however, with empyreumatic oily products, which give it a powerful odour and a dark colour The residual pitch contains much pine-resin, and thus differs from the solid portion of the hard wood-tar so frequently mentioned.

Volatile Principles of Coal-Tar.

Coal-tar yields on distillation a large quantity of thin, dark-coloured, volatile oil, which, when agitated with dilute sulphuric acid to remove ammonia, and twice rectified with water, becomes nearly colourless: it is very volatile, lighter than water, very inflammable, and possesses in a high degree the property of dissolving caoutchouc, on which account it is very extensively used in the manufacture of water-proof fabrics containing that material.

This coal-oil is a mixture of a great variety of liquids and solids dissolved in the oil. By the action of acids and alkalis, this mixture may be conveniently divided into three separate groups. (1) A group of basic compounds soluble in acids; (2) an acid portion soluble in alkalis; and (3) a group of neutral constituents.

The basic constituents form but a small part of coal-tar-oil. They are extracted by agitating successively large quantities of the oil with hydrochloric acid, and afterwards distilling the acid watery liquid obtained with excess of hydrate of lime. The bases thus obtained consist chiefly of picoline (see page 465), aniline (see page 459), and leucoline (see page 464), and are separated by distillation; these three compounds boiling at very different temperatures.

The acid portion of coal-tar-oil consists essentially of carbolic acid or phenol.

CARBOLIC ACID; PHENOL.—Common coal tar-oil is agitated with a mixture of hydrate of lime and water, the whole being left for a considerable time; the aqueous liquid is then separated from the undissolved oil, decomposed by hydrochloric acid, and the oily product obtained purified by cautious distillation, the first third only being collected. Or crude coal-oil is subjected to distillation in a retort furnished with a thermometer, and the portion which passes over between the temperatures of 300°—400° (149°—204° 5C) collected apart. This product is then mixed with a hot strong solution of caustic potassa, and left to stand; a whitish, somewhat crystalline, pasty mass is obtained, which by the action of water is resolved into a light oily liquid and a dense alkaline solution. The latter is withdrawn by a syphon, decomposed by hydrochloric acid, and the separated oil purified by contact with chloride of calcium and re-distillation. Lastly, it is exposed to a low temperature, and the crystals formed drained from the mother-liquor and carefully preserved from the air.

Pure carbolic acid forms long colourless prismatic needles, which melt at 95° (35°C) to an oily liquid, boiling at 370° (180°C), and greatly resembling kreosote[1] in many particulars, having a very penetrating odour and burning taste, and attacking the skin of the lips. Its sp. gr. is 1·065. It is slightly soluble in water, freely in alcohol and ether, and has no acid reaction to test-paper. The crystals absorb moisture with avidity, and liquefy. It coagulates albumin. Sulphur and iodine dissolve in it; nitric acid, chlorine, and bromine attack it with energy. Carbolic acid contains $C_{12}H_6O,HO$.

In its chemical deportment carbolic acid stands very near the alcohols, a fact to which allusion has been made already in former sections (see pages 399 and 401); we may assume in it a compound radical, *phenyl*, $C_{12}H_5$=Pyl, analogous to ethyl, when carbolic acid becomes Pyl O,HO, or hydrated oxide of phenyl.

With sulphuric acid, hydrate of oxide of phenyl forms the compound acid, *sulphophenic acid*, $C_{12}H_5O,2SO_3,HO$=Pyl O,$2SO_3$,HO, which assumes a syrupy

[1] *A great deal of the kreosote which occurs in commerce is, in fact, nothing but more or less pure carbolic acid.*

state in the dry vacuum. This acid closely corresponds to sulphovinic acid (see page 358). The baryta-salt crystallizes from alcohol in minute needles.

Phenyl-alcohol dissolves potassium with evolution of hydrogen, a compound $C_{12}H_5O,KO$ being produced, which is analogous to the substance formed in a similar manner from common alcohol (see page 347). On heating this potassa-compound with iodide of methyl, ethyl, or amyl, a series of double ethers are produced represented by the following formulæ:—

Oxide of phenyl and methyl	PylO,MeO	$= C_{12}H_5O,C_2H_3O$	$= C_{14}H_8O_2$
Oxide of phenyl and ethyl	PylO,AeO	$= C_{12}H_5O,C_4H_5O$	$= C_{16}H_{10}O_2$
Oxide of phenyl and amyl	PylO,AyO	$= C_{12}H_5O,C_{10}H_{11}O$	$= C_{22}H_{16}O_2$

Those substances also described by the names *anisol* (because it is likewise produced by the distillation of anisic acid (see page 491), *phenetol* and *phenamylol* are evidently analogous to the compounds of oxide of methyl with those of ethyl and amyl, which have been mentioned in pages 382 and 389.

A *chloride of phenyl*, $C_{12}H_5Cl$=PylCl, has been produced by the action of pentachloride of phosphorus upon hydrated oxide of phenyl. This compound, however, which is a heavy oil, is but very imperfectly known.

Cyanide of phenyl, $C_{14}H_5N=C_{12}H_5C_2N$=PylCy, has not yet been produced from phenyl-alcohol directly. The substance, however, which has been described under the name of benzonitrile (page 401), is both by composition and deportment *cyanide of phenyl*, perfectly analogous to cyanide of ethyl (see page 354). Boiled with potassa it is converted into ammonia and benzoic acid, cyanide of ethyl furnishing ammonia and propionic acid. Starting from this decomposition, benzoic acid may be viewed as *phenyl-oxalic* acid $C_{14}H_5O_3,HO=C_{12}H_5,C_2O_3,HO$, just as propionic acid may be regarded as ethyl-oxalic acid (see page 392).

Hydrated oxide of phenyl when treated with chloride of benzoyl (see page 400) yields hydrochloric acid and a white fusible crystalline compound which is *benzoate of phenyl* $C_{12}H_5O,C_{14}H_5O_3$=PylO,BzO, analogous to benzoate of ethyl; when heated with ammonia, phenyl-alcohol yields *aniline* $C_{12}H_7N= C_{12}H_5H_2N=PylH_2N$ (*phenylamine*), the ethylamine of the phenyl-series (see page 459).

The following table gives a synopsis of the phenyl-compounds, which have been placed in juxtaposition with the corresponding terms of the ethyl-series:—

Phenyl-alcohol	PylO,HO	AeO,HO	Ethyl-alcohol
Oxide of phenyl-potassa	PylO,KO	AeO,KO	Oxide of ethyl-potassa
Sulphophenic acid	$PylO,2SO_3,HO$	$AeO,2SO_3,HO$	Sulphovinic acid
		AeO	Oxide of ethyl
Chloride of phenyl	PylCl(?)	Aecl	Chloride of ethyl
Cyanide of phenyl (benzonitrile)	PylCy	AeCy	Cyanide of ethyl (propio nitrile)
Benzoate of phenyl	$PylO,PylC_2O_3$	AeO,Ae,C_2O_3	Propionate of ethyl
Phenyl-amine (aniline	NH_2Pyl	NH_2Ae	Ethylamine
Phenyl-urea	$C_2(H_3Pyl)NO_2$	$C_2(H_3Ae)NO_2$	Ethyl-urea.

Chlorophenisic acid. — This is the characteristic and principal product of the action of chlorine on hydrate of oxide of phenyl. The pure substance is not necessary for the preparation of this body, those portions of crude coal-oil which boil between 360°—400° (182°·2—204°·5C) answering very well. The oil is saturated with chlorine, and distilled in the open air, the first and last portions being rejected; the product is again treated with

Volatile Principles of Coal-Tar.

Coal-tar yields on distillation a large quantity
volatile oil, which, when agitated with dilute sul
monia, and twice rectified with water, becomes
volatile, lighter than water, very inflammable, a
the property of dissolving caoutchouc, on wh
sively used in the manufacture of water
material.

This coal-oil is a mixture of a great var
in the oil. By the action of acids and
niently divided into three separate gro
soluble in acids; (2) an acid portion
neutral constituents.

The basic constituents form but
tracted by agitating successively
acid, and afterwards distilling
of hydrate of lime. The base
page 465), aniline (see page
separated by distillation; t
temperatures.

The acid portion of c
phenol.

CARBOLIC ACID; PHEN
of hydrate of lime and
the aqueous liquid is
by hydrochloric acid.
tillation, the first th
to distillation in a
which passes over
collected apart.
caustic potassa,
mass is obtained
liquid and a de
decomposed by
with chloride
temperature,
carefully pr

Pure carl
95 (35°C)
kreosote[1] i
taste, and
soluble in
test-paper
agulates
and bron

In its
fact to v
399 and
analogo
of phen

With
sulphop

ned and dissolved
ngly soluble chloro-
ed in pure water, de-
distilled.
rless, silky needles, which
ng, persistent, and charac-
ater, but dissolves freely in
c acid. It slowly sublimes at
ullition when strongly heated.
ts, and contains $C_{12}(H_2Cl_3)O.HO$.
e an analogous acid richer in chlo-
usic acid, and contains $C_{12}Cl_5O,HO$.
gous means, and possesses a consti-
g those of the chlorine-compound.
phenyl-alcohol with very dilute nitric
tained, soluble in ammonia and potassa,
salt. This substance is *nitrophenasic acid*.
Nitrophenesic and nitrophenisic acids may
which is employed in the preparation of
carefully mixed in a large open vessel with
of ordinary nitric acid. The action is very
substance produced is slightly washed with
e ammonia, and filtered hot. A brown mass
is preserved to prepare nitrophenisic acid, and
oling a very impure ammoniacal salt of nitro-
es several successive crystallizations, after which
cid and the product crystallized from alcohol.
s blonde-coloured prismatic crystals, very spar-
ng water, but freely soluble in alcohol. It has no
feeble, becomes after a short time very bitter. At
d on cooling crystallizes. In very small quantity
at decomposition, but when briskly heated it often
ntly. The salts of this acid are yellow or orange
y are mostly soluble in water, and detonate feebly
d contains $C_{12}H_3N_2O_9,HO=C_{12}H_3(NO_4)_2O,HO$. Nitro-
cal with picric or carbazotic acid (see page 473). It
a great economy from impure nitrophenesic acid, or
insoluble in dilute ammonia already referred to. It is
similar to that employed in the case of the prece
enisic acid contains $C_{12}H_2N_3O_{13},HO=C_{12}H_2(NO_4)_3O,HO$.

ile exhibits the relation of these substitution-products:—

nol	$C_{12}H_5$	O,HO = Phenol
asic acid	$C_{12}(H_2Cl_3)$	O,HO = Trichlorophenol
sic acid	$C_{12}(H_4NO_4)$	O,HO = Nitrophenol
esic acid	$C_{12}(H_3[NO_4]_2)$	O,HO = Binitrophenol
enisic acid	$C_{12}(H_2[NO_4]_3)$	O,HO = Trinitrophenol.

portion of coal-tar naphtha consists of a great variety of hy-
y liquid, partly solid. The liquid hydrocarbons have been
ed (see pages 398 and 403). They are chiefly *benzol*, t
and *cymol*.[2] The solid hydrocarbons are *naphthalin* and
ther with several similar substances less perfectly known

[1] A gr
less pur

m. et Phys. 3d series, iii. 195.

[2] e hydrocarbons have been lately found by M. Cahours in the oily liquids
water from commercial wood-spirits (see page 5).

...stillation of coal-tar, the last portion of ...part and left to stand, a quantity of ... is principally composed of the ...antity may be obtained by pushing ... vessel begin to char; the naphthalin ... dark-coloured and very impure. By ...epeated, it is obtained perfectly white. ..., colourless, transparent, brilliant, crys... peculiar odour, which has been compared ...halin melts at 176° (80°C) to a clear, colour... on cooling; it boils at 418° (211°·6C), and ...ty is 4·528. When strongly heated in the air, ... red and very smoky light. It is insoluble in ... slight degree at the boiling temperature; alcohol ...ily; a hot saturated alcoholic solution deposits fine ...cooling.

...d by analysis to contain $C_{10}H_4$ or $C_{20}H_8$. ...ives in warm concentrated sulphuric acid, forming a red ...en diluted with water, and saturated with carbonate of ...alts of at least two distinct acids, analogous to sulphovinic ... these, the *sulphonaphthalic acid* of Mr Faraday, crystallises ...queous solution in small white scales, which are but sparingly ...he acid. The free acid is obtained in the usual manner by de...g the baryta-salt with sulphuric acid; it forms a colourless, crys... brittle mass, of acid, metallic taste, very deliquescent, and very solu... water. The second baryta-salt is still less soluble than the preceding. ...composition of sulphonaphthalic acid is $C_{20}H_7S_2O_5,HO$.

Fuming nitric acid at a high temperature attacks naphthalin; the products are numerous, and have been attentively studied by M. Laurent. The same chemist has described a long series of curious products of the action of chlorine on naphthalin. Nitric acid gives rise to a great number of nitro-substitutes, the most interesting of which, is the compound known by the name *nitronaphthalase*, which, when submitted to Zinin's process, is converted into *naphthalidine* (see page 462). Among the derivatives of naphthalin, a compound deserves to be mentioned, which has been described under the name of *phthalic acid*. This acid has not yet been produced directly from naphthalin, but may be obtained by boiling one of the products of the action of chlorine upon naphthalin, namely, the tetrachloride of naphthalin ($C_{20}H_8Cl_4$) with nitric acid. The same substance is formed by submitting alizarin to the action of nitric acid.

Phthalic acid crystallizes in yellow plates; it is but slightly soluble in cold water, but dissolves freely in alcohol and ether. Phthalic acid is bibasic, and contains $C_{16}H_4O_6.2HO$; when heated it loses 2 eq. of water, and becomes $C_{16}H_4O_6$. Treated with fuming nitric acid it yields a nitro-acid, nitro-phthalic acid, $C_{16}(H_3NO_4)\,O_6,\,2HO$. When distilled with baryta it is converted into benzol:—

$$\underbrace{C_{16}H_6O_8+4BaO}_{\text{Phthalic acid.}} = 4(BaOCO_2)+\underbrace{C_{12}H_6}_{\text{Benzol.}}$$

The formation of phthalic acid from alizarin has established a most interesting connection between the naphthalin and alizarin-series. It would be of great interest if naphthalin, which is produced in enormous quantities in the manufacture of coal-gas, but has not yet found any useful application, could be converted by chemical processes into alizarin. That there is a hope of such a conversion being possible, is even now pointed out by the close

analogy of one of the chlorine products of naphthalin, of *chloronaphthalic* acid, both in composition and properties with *alizarin*. This substance contains $C_{20}(H_5Cl)O_6$, and may be viewed as chloralizarin :—

Alizarin..	$C_{20}\,H_6\,O_6$
Chloronaphthalic acid	$C_{20}(H_5Cl)O_6$.

Chloronaphthalic acid produces most beautifully coloured compounds with the metallic oxides.

The history of the formation of naphthalin is rather interesting; it is perhaps the most stable of all the more complex compounds of carbon and hydrogen : in a vessel void of free oxygen it may be heated to any extent without decomposition ; and, indeed, where other carburets of hydrogen are exposed to a very high temperature, as by passing in vapour through a red-hot porcelain tube, a certain quantity of naphthalin is almost invariably produced. Hence its presence in coal and other tar is mainly dependent upon the temperature at which the destructive distillation of the organic substance has been conducted. Lampblack very frequently contains naphthalin thus accidentally produced.

PARANAPHTHALIN.—This substance occurs in the naphthalin of coal-tar, and is separated by the use of alcohol, in which ordinary naphthalin is freely soluble, whilst paranaphthalin is almost totally insoluble ; in other respects it much resembles naphthalin. The crystals obtained by sublimation are, however, usually smaller and less distinct. It melts at 356° (180°C), and boils at 570° (299°C), or above. Its best solvent is oil of turpentin. Paranaphthalin has the same composition as naphthalin itself ; the density of its vapour is, however, different, viz., 6·741. Its composition may be represented by the formula $C_{30}H_{12}$.

PETROLEUM, NAPHTHA, AND OTHER ALLIED SUBSTANCES.

Pit-coal, *lignite* or *brown coal*, *jet*, *bitumen* of various kinds, *petroleum* or *rock-oil*, and *naphtha*, and a few other allied substances more rarely met with, are looked upon as products of the decomposition of organic matter, especially vegetable matter, beneath the surface of the earth, in situations where the conditions of contact with water, and nearly total exclusion of atmospheric air, are fulfilled. Deposited at the bottom of seas, lakes, or rivers, and subsequently covered up by accumulations of clay and sand, hereafter destined to become shale and gritstone, the organic tissue undergoes a kind of fermentation, by which the bodies in question, or certain of them, are slowly produced. Carbonic acid and light carbonetted hydrogen are by-products of the reaction ; hence their frequent disengagement, the first from beds of lignite, and the second from the farther advanced and more perfect coal.

The vegetable origin of coal has been placed beyond doubt by microscopic research ; vegetable structure can be thus detected even in the most massive and perfect varieties of coal when cut into thin slices. In coal of inferior quality, much mixed with earthy matter, it is evident to the eye ; the leaves of ferns, reeds, and other succulent plants, more or less resembling those of the tropics, are found in a compressed state between the layers of shale or slaty clay, preserved in the most beautiful manner, but entirely converted into bituminous coal. The coal-mines of Europe, and particularly those of our own country, furnish an almost complete fossil-flora ; a history of many of the now lost species which once decorated the surface of the earth.

In the lignites the woody structure is much more obvious. Beds of this material are found in very many of the newer strata, above the true coal, to which they are consequently posterior. As an article of fuel, brown-coal

omparatively small value; it resembles peat, giving but little flame and ting a disagreeable, pungent smell.

it, used for making black ornaments, is a variety of lignite.

he true bitumens are destitute of all organic structure; they appear to arisen from coal or lignite by the action of subterranean heat, and closely resemble some of the products yielded by the destructive distion of those bodies. They are very numerous, and have yet been but erfectly studied.

. *Mineral pitch*, or *compact bitumen*, the *asphaltum* or *Jew's pitch* of some hors. — This substance occurs abundantly in many parts of the world; in the neighbourhood of the Dead Sea in Judea; in Trinidad, in the ious *pitch lake*, and elsewhere. It generally resembles in aspect common h, being a little heavier than water, easily melted, very inflammable, and ning with a red, smoky flame. It consists principally of a substance led by M. Boussingault *asphaltene*, composed of $C_{20}H_{16}O_3$. It is worthy remark, that M. Laurent found paranaphthalin in a native mineral ch.

2. *Mineral tar* seems to be essentially a solution of asphaltene in an oily id called *petrolene*. This has a pale yellow colour and peculiar odour; it lighter than water, very combustible, and has a high boiling point. It the same composition as the oils of turpentin and lemon-peel, namely H_8. Asphaltene contains, consequently, the elements of petrolene, toher with a quantity of oxygen, and probably arises from the oxidation of t substance.

3. *Elastic bitumen; mineral caoutchouc.* — This curious substance has only n found in three places; in a lead-mine at Castleton, in Derbyshire; at ntrelais, in France; and in the State of Massachusetts. In the two latter alities it occurs in the coal-series. It is fusible, and resembles in many pects the other bitumens.

Under the names *petroleum* and *naphtha* are arranged various mineral oils ich are observed in many places to issue from the earth, often in conrable abundance. There is every reason to suppose that these owe their gin to the action of internal heat upon beds of coal, as they are usually nd in connection with such. The term *naphtha* is given to the thinner purer varieties of rock-oil, which are sometimes nearly colourless; the ker and more viscid liquids bear the name of *petroleum*.

ome of the most noted localities of these substances are the following:— north-west side of the Caspian Sea, near Baku, where beds of marl are nd saturated with naphtha. Wells are sunk to the depth of about 30 , in which naphtha and water collect, and are easily separated. In some ts of this district so much combustible gas or vapour rises from the und, that when set on fire, it continues burning, and even affords heat for nomical purposes. A large quantity of an impure variety of petroleum ies from the Birman territory in the East Indies: the country consists of dy clay, resting on a series of alternate strata of sandstone and shale. neath these occurs a bed of pale blue shale loaded with petroleum, which immediately on coal. A petroleum-spring exists at Colebrook Dale, in opshire. The sea near the Cape de Verde Islands has been seen covered h a film of rock-oil. The finest specimens of naphtha are furnished by ly, where it occurs in several places.

In proof of the origin attributed to these substances, an experiment of . Reichenbach may be cited, who, by distilling with water about 100 lb. of -coal, obtained nearly 2 ounces of an oily liquid exactly resembling the tural naphtha of Amiano, in the Duchy of Parma.

The variations of colour and consistence in different specimens of these dies *certainly* depends in great measure upon the presence of pitchy and

fatty substances dissolved in the more fluid oil. Dr. Gregory found paraffin in petroleum from Rangoon.

The boiling-point of rock-oil varies from about 180° to near 600° (82°·2 to 315°·5C); a thermometer inserted into a retort in which the oil is undergoing distillation, never shows for any length of time a constant temperature. Hence it is inferred to be a mixture of several different substances. Neither do the different varieties of naphtha give similar results on analysis; they are all, however, carbides of hydrogen. The use of these substances in the places where they abound is tolerably extensive; they often serve the inhabitants for fuel, light, &c. To the chemist pure naphtha is valuable, as offering facilities for the preservation of the more oxidable metals, as potassium and sodium.

The following are of rarer occurrence:—

Retinite, or *Retinasphalt*, is a kind of fossil resin met with in brown coal; it has a yellow or reddish colour, is fusible and inflammable, and readily dissolved in great part by alcohol. The soluble portion has been called *retinic acid* by Prof. Johnston. *Hatchetin* is a somewhat similar substance met with in mineral coal at Merthyr-Tydvil, and also near Loch Fyne, in Scotland. *Idrialin* is found associated with native cinnabar, and is extracted from the ore by oil of turpentin, in which it dissolves. It is a white, crystalline substance, scarcely volatile without decomposition, but slightly soluble in alcohol and ether, and composed of $C_{42}H_{14}O$; it is generally associated with a hydrocarbon *idryl*, which contains $C_{42}H_{14}$.

Ozokerite, or *fossil wax*, is found in Moldavia, in a layer of bituminous shale; it is brownish and has a somewhat pearly appearance; it is fusible below 212° (100°C), and soluble with difficulty in alcohol and ether, but easily in oil of turpentin. It appears to contain more than one definite principle.

APPENDIX.

HYDROMETER TABLES.

COMPARISON OF THE DEGREES OF BAUMÉ'S HYDROMETER WITH THE REAL SPECIFIC GRAVITIES.

1. *For liquids heavier than water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	26	1·206	52	1·520
1	1·007	27	1·216	53	1·535
2	1·013	28	1·225	54	1·551
3	1·020	29	1·235	55	1·567
4	1·027	30	1·245	56	1·583
5	1·034	31	1·256	57	1·600
6	1·041	32	1·267	58	1·617
7	1·048	33	1·277	59	1·634
8	1·056	34	1·288	60	1·652
9	1·063	35	1·299	61	1·670
10	1·070	36	1·310	62	1·689
11	1·078	37	1·321	63	1·708
12	1·085	38	1·333	64	1·727
13	1·094	39	1·345	65	1·747
14	1·101	40	1·357	66	1·767
15	1·109	41	1·369	67	1·788
16	1·118	42	1·381	68	1·809
17	1·126	43	1·395	69	1·831
18	1·134	44	1·407	70	1·854
19	1·143	45	1·420	71	1·877
20	1·152	46	1·434	72	1·900
21	1·160	47	1·448	73	1·924
22	1·169	48	1·462	74	1·949
23	1·178	49	1·476	75	1·974
24	1·188	50	1·490	76	2·000
25	1·197	51	1·495		

2. *Baumé's Hydrometer for liquids lighter than water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	27	0·896	44	0·811
11	0·993	28	0·890	45	0·807
12	0·986	29	0·885	46	0·802
13	0·980	30	0·880	47	0·798
14	0·973	31	0·874	48	0·794
15	0·967	32	0·869	49	0·789
16	0·960	33	0·864	50	0·785
17	0·954	34	0·859	51	0·781
18	0·948	35	0·854	52	0·777
19	0·942	36	0·849	53	0·773
20	0·936	37	0·844	54	0·768
21	0·930	38	0·839	55	0·764
22	0·924	39	0·834	56	0·760
23	0·918	40	0·830	57	0·757
24	0·913	41	0·825	58	0·753
25	0·907	42	0·820	59	0·749
26	0·901	43	0·816	60	0·745

These two tables are on the authority of M. Francœur; they are taken om the *Handwörterbuch der Chemie* of Liebig and Poggendorff. Baumé's ydrometer is very commonly used on the Continent, especially for liquids eavier than water. For lighter liquids, the hydrometer of Cartier is often nployed in France. Cartier's degrees differ but little from those of aumé.

In the United Kingdom, Twaddell's hydrometer is a good deal used for ense liquids. This instrument is so graduated that the real sp. gr. can be educed by an extremely simple method from the degree of the hydrometer, amely, by multiplying the latter by 5, and adding 1000; the sum is the). gr., water being 1000. Thus 10° Twaddell indicates a sp. gr. of 1050, : 1·05; 90° Twaddell, 1450, or 1·45.

In the Customs and Excise, Sike's hydrometer is used.

ABSTRACT

OF DR. DALTON'S TABLE OF THE ELASTIC FORCE OF VAPOUR OF WATER AT DIFFERENT TEMPERATURES, EXPRESSED IN INCHES OF MERCURY.

Temperature.		Force.	Temperature.		Force.	Temperature.		Force.
Fah.	Cent.		Fah.	Cent.		Fah.	Cent.	
32°	0°·0	0·200	57°	13°·88	0·474	90°	32°·2	1·36
33	0°·55	0·207	58	14°·4	0·490	95	35°	1·58
34	1°·1	0·214	59	15°	0·507	100	37°·77	1·86
35	1°·66	0·221	60	15°·5	0·524	105	40° 5	2·16
36	2°·2	0·229	61	16°·1	0 542	110	43° 3	2·53
37	2°·77	0·237	62	16°·66	0·560	115	46°·1	2·92
38	3°·3	0 245	63	17°·2	0 578	120	48°·88	3·33
39	3°·88	0 254	64	17°·77	0·597	125	51°·66	3·75
40	4°·4	0·263	65	18° 3	0·616	130	54°·4	4·34
41	5°	0·273	66	18°·88	0·635	135	57°·2	5·00
42	5°·55	0·283	67	19°·4	0·665	140	60°	5·74
43	6°·1	0·294	68	20°	0·676	145	62°·77	6·53
44	6°·66	0·305	69	20°·55	0·698	150	65°·5	7 42
45	7°·2	0·316	70	21°·1	0·721	160	71°·1	9·46
46	7° 77	0·328	71	21°·66	0·745	170	76° 66	12·13
47	8°·3	0 339	72	22°·2	0·770	180	82°·2	15·15
48	8°·88	0 351	73	22°·77	0·796	190	87° 77	19 00
49	9°·4	0·363	74	23° 3	0 823	200	93°·3	23 64
50	10°	0·375	75	23°·88	0 851	210	98° 88	28·84
51	10°·55	0·388	76	24°·4	0 880	212	100°	30·00
52	11°·1	0·401	77	25°	0·910	220	104°·4	34·99
53	11°·66	0·415	78	25°·5	0·940	230	110°	41·75
54	12° 2	0·429	79	26°·1	0 971	240	115°·5	49·67
55	12°·77	0·443	80	26°·66	1·000	250	121°·1	58·21
56	13°·3	0·458	85	29°·44	1·170	300	148°·88	111·81

TABLE

F THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL IN 100 PARTS OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES. (FOWNES.)

Sp. Gr. at 60° (15°·5C).	Per cent. of real Alcohol.	Sp. Gr. at 60° (15°·5C.)	Per cent. of real Alcohol.	Sp. Gr. at 60° (15°·5C).	Per cent. of real Alcohol.
0·9991	0·5	0·9511	34	0·8769	68
0·9981	1	0·9490	35	0·8745	69
0·9965	2	0·9470	36	0·8721	70
0·9947	3	0·9452	37	0·8696	71
0·9930	4	0·9434	38	0·8672	72
0·9914	5	0·9416	39	0·8649	73
0·9898	6	0·9396	40	0·8625	74
0·9884	7	0·9376	41	0·8603	75
0·9869	8	0·9356	42	0·8581	76
0·9855	9	0·9335	43	0·8557	77
0·9841	10	0·9314	44	0·8533	78
0·9828	11	0·9292	45	0·8508	79
0·9815	12	0·9270	46	0·8483	80
0·9802	13	0·9249	47	0·8459	81
0·9789	14	0·9228	48	0·8434	82
0·9778	15	0·9206	49	0·8408	83
0·9766	16	0·9184	50	0·8382	84
0·9753	17	0·9160	51	0·8357	85
0·9741	18	0·9135	52	0·8331	86
0·9728	19	0·9113	53	0·8305	87
0·9716	20	0·9090	54	0·8279	88
0·9704	21	0·9069	55	0·8254	89
0·9691	22	0·9047	56	0·8228	90
0·9678	23	0·9025	57	0·8199	91
0·9665	24	0·9001	58	0·8172	92
0·9652	25	0·8979	59	0·8145	93
0·9638	26	0·8956	60	0·8118	94
0·9623	27	0·8932	61	0·8089	95
0·9609	28	0·8908	62	0·8061	96
0·9593	29	0·8886	63	0·8031	97
0·9578	30	0·8863	64	0·8001	98
0·9560	31	0·8840	65	0·7969	99
0·9544	32	0·8816	66	0·7938	100
0·9528	33	0·8798	67		

F ANALYSES

E SARATOGA CONGRESS SPRING OF AMERICA.

	Kissengen. Ragozi.	Marienbad. Kreutbr.	Auschowitz. Ferdinands-Brunnen.	Eger. Franzens-Brunnen.
	......	5·3499	4·5976	3·8914
	......	0·0858	0·0507	0·0282
	......	......	......	......
	0·0592	0·0028	0·0040	0·0023
	4·8180	2·9509	3·0085	1·3501
	1·3185	2·0390	2·2867	0·5040
	0·0121	2·0288	0·0692	0·0322
	0·1397	0·1319	0·2995	0·1762
	......	......	......	0·0172
	......	......	0·0040	0·0092
	1·2540	......	......	......
	......	28·5868	16·9022	18·3785
	......	......	......	......
	5·5485	......	......	......
	......	......	......	......
	......	......	......	......
	......	......	......	......
	0·0864	......	......	......
	......	......	......	......
	39·3733	10·1727	6·7472	6·9229
	......	......	......	......
	......	......	......	......
	3·6599	......	......	......
	......	......	......	......
	......	......	......	......
	0·3331	......	......	......
	......	......	......	......
	......	......	......	......
	......	0·0023	......	......
	0·1609	0·2908	0·5023	0·3548
	56·7136	51·6417	34·4719	31·6670
	96	105	146	154
C)	53° (11°·6C)	53° (11°·6C)	49° (9°·5C)	54° (12°·2C)
r.	Struve.	Berzelius.	Steinman.	Berzelius.

DR. SCHWEITZER'S

OF THE PRINCIPAL MINERAL WATERS OF GERMANY

Grains of Anhydrous Ingredients in One Pound Troy.	Carlsbad.	Ems.	Schlesischer. Obersalz-Brunnen.
Carbonate of Soda..........	7·2712	8·0625	7·6211
Ditto of Lithia................	0·0150	0·0405	......
Ditto of Baryta................	......	0·0022	......
Ditto of Strontia	0·0055	0·0080	0·0170
Ditto of Lime..................	1·7775	0·8555	1·5404
Ditto of Magnesia	1·0275	0·5915	1·5496
Ditto (proto) of Manganese	0·0048	0·0028	0·0026
Ditto (proto) of Iron	0·0208	0·0120	0·0856
Sub-Phos. of Lime............	0·0012	......	......
Ditto of Alumina..............	0·0019	0·0014	......
Sulphate of Potassa..........	......	0·4050	0·3160
Ditto of Soda..................	14·9019	......	2·5106
Ditto of Lithia................	......	......	......
Ditto of Lime..........	......	......	......
Ditto of Strontia..............	......	......	......
Ditto of Magnesia............	......	......	......
Nitr. of Magnesia..............	......	......	......
Chlor. of Ammonium..........	......	......	0·0164
Ditto of Potassium	......	0·0338	......
Ditto of Sodium................	5·9820	5·7255	0·8682
Ditto of Lithium..............	......	......	......
Ditto of Calcium	......	......	......
Ditto of Magnesium..........	......	......	......
Ditto of Barium................	......	......	......
Ditto of Strontium	......	......	......
Bromide of Sodium............	......	......	0·0051
Iodide of Sodium..............	......	......	......
Fluoride of Calcium..........	0·0184	0·0014	......
Alumina	......	......	......
Silica..............................	0·4329	0·3104	0·2423
Total	31·4606	16·0525	14·7309
Carbonic Acid Gas in 100 cubic inches	58	51	98
Temperature	Sprud. 165° (73°·8C) Neub. 138° (58°·8C) Mühl. 128° (53°·3C) Ther. 122° (50°C)	Kess. 117° (47°·2C) Krän. 84° (28°·8C)	58° (14°·5C
Analyzed by	Berzelius.	Struve.	Struve.

TABLE OF ANALYSES

AND OF THE SARATOGA CONGRESS SPRING OF AMERICA.

Saratoga Congress Spring.	Kissengen. Ragozi.	Marienbad. Kreutbr.	Auschowitz. Ferdinands-Brunnen.	Eger. Franzens-Brunnen.
0·8261	......	5·3499	4·5976	3·8914
......	......	0·0858	0·0507	0·0282
......	......	......	......	......
0·0672	0·0592	0·0028	0·0040	0·0028
5·8531	4·8180	2·9509	3·0085	1·3501
4·1155	1·3185	2·0390	2·2867	0·5040
0·0202	0·0121	2·0288	0·0692	0·0322
0·0173	0·1397	0·1319	0·2995	0·1762
......	......	......	......	0·0172
......	......	......	0·0040	0·0092
0·1379	1·2540	......	......	......
......	......	28·5868	16·9022	18·3785
......	......	......	......	......
......	5·5485	......	......	......
......	......	......	......	......
......	......	......	......	......
0·1004	......	......	......	......
0·0326	0·0864	......	......	......
1·6256	......	......	......	......
19·6653	39·3733	10·1727	6·7472	6·9229
......	......	......	......	......
......	......	......	......	......
......	3·6599	......	......	......
......	......	......	......	......
......	......	......	......	......
0·1618	0·3331	......	......	......
0·0046	......	......	......	......
......	......	......	......	......
0·0069	......	0·0023	......	......
0·1112	0·1609	0·2908	0·5023	0·3548
32·7452	56·7186	51·6417	34·4719	31·6670
114	96	105	146	154
50° (10°C)	53° (11°·6C)	53° (11°·6C)	49° (9°·5C)	54° (12°·2C)
Schweitzer.	*Struve.*	Berzelius.	Steinman.	Berzelius.

DR. SCHWEITZER'S

OF THE PRINCIPAL MINERAL WATERS OF GERMANY

Grains of Anhydrous Ingredients in One Pound Troy.	Pyrmont.	Spa Pouhon.	Fachingen.
Carbonate of Soda..........	......	0·5581	12·3328
Ditto of Lithia..................	......	......	......
Ditto of Baryta................	......	......	......
Ditto of Strontia..............	......	......	......
Ditto of Lime.................	4·7781	0·7387	1·5667
Ditto of Magnesia...........		0·8421	1·2963
Ditto (proto) of Manganese		0·0389	......
Ditto (proto) of Iron........		0·2818	......
Sub-Phos. of Lime..........		0·0102	0·0061
Ditto of Alumina..............		0 0064	......
Sulphate of Potassa.........		0·0593	......
Ditto of Soda..................		0·0281	0·1267
Ditto of Lithia................		......	......
Ditto of Lime..................		......	......
Ditto of Strontia.............		......	......
Ditto of Magnesia...........		......	......
Nitr. of Magnesia...........		......	......
Chlor. of Ammonium.......		......	......
Ditto of Potassium..........		......	......
Ditto of Sodium..............	......	0·3371	3·2337
Ditto of Lithium..............	......	......	......
Ditto of Calcium..............	......	......	......
Ditto of Magnesium.........	0·8450	......	......
Ditto of Barium..............	......	......	......
Ditto of Strontium..........	......	......	......
Bromide of Sodium..........	......	......	......
Iodide of Sodium............	......	......	......
Fluoride of Calcium.........	......	......	......
Alumina..........................	......	......	......
Silica.............................	0 3727	0·3789	0·0657
Total.............................	15·4221	3·2691	18·9300
Carbonic Acid Gas in 100 cubic inches..............	160	136	135
Temperature (F.)............	56° (13°·3C)	50° (10°C)	50° (10°C)
Analyzed by....................	Struve.	Struve.	Bischoff.

ABLE OF ANALYSES

ND OF THE SARATOGA CONGRESS SPRING OF AMERICA, *continued.*

Selters.	Seidschütz.	Püllna.	Kreuznach. Elisen-Brunnen.	Adelheids-Quelle.
4·6162	......	......	......	5·2443
......	......	......	......	0·0902
0·0014	......	......	......	0·0024
0·0144	......	......	......	0·0387
1·4004	5·1045	0·5775	0·2058	0·4703
1·5000	0·8235	4·8045	1·1812	0·2980
......	0·0032	......	0·0072	0·0012
......	0·0095	......	0·1495	0·0121
0·0007	0·0117	0·0026	......	......
0·0020	0·0088	......	......	......
0·2978	3·6705	3·6000	......	0·0066
......	17·6220	92·8500	......	......
......	......	......	......	......
......	1·1287	1·9500	......	......
......	0·0347	......	......	......
......	62·3535	69·8145	......	......
......	5·9302	......	......	......
......	......	......	......	......
0·2685	......	......	0·7287	0·1845
12·9690	......	......	54·6917	28·4608
......	......	......	0·0562	......
......	......	......	9·7358	......
......	1·2225	14·7495	......	......
......	......	......	0·2366	......
......	......	......	0·5494	......
......	......	......	0·2304	0·3060
......	......	......	0·0024	0·1500
0·0013	......	......	......	......
......	......	......	0·0086	0·0166
0·2265	0·0900	0·1320	0·2355	0·1922
21·2982	98·0133	188·4806	68·0190	35·4739
126	20	7	12	10
58° (14°·5C)	58° (14°·5C)	58° (14°·5C)	47° (8°·3C)	58° (14°·5C)
Struve.	Struve.	Struve.	Struve.	Struve.

WEIGHTS AND MEASURES

480·0	grains Tr[illegible]	[illegible]oz. Troy.
437·5	"	[illegible] oz. Avoirdupoids.
7000·0	"	[illegible] lb. Avoirdupoids.
5760·0	"	[illegible] lb. Troy.

The imperial gallon contains of [illegible]t 60° (15°·5C)	70,000·	grains
The pint ($\frac{1}{8}$ of gallon)..........[illegible]....................	8,750·	"
The fluid-ounce ($\frac{1}{20}$ of pint)....[illegible]....................	437·5	"

The pint equal[illegible] cubic inches.

The French *kilogramme* = 15,433·6 grains, or 2·679 lb. Troy, or 2·205 lb. avoirdupoids.

The *grammme*	=	15·4336	grains.
" *decigramme*	=	1·5434	"
" *centigramme*	=	0·1543	"
" *milligramme*	=	0·0154	"

The *mètre* of France	=	39·37	inches.
" *decimètre*	=	3·937	"
" *centimètre*	=	0·394	"
" *millimètre*	=	0·0394	"

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